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(71) 出願人（米国を除くすべての指定国について）
日本電気株式会社(NEC CORPORATION)[JP/JP]
〒108-8001 東京都港区芝五丁目7番1号 Tokyo, (JP)
(72) 発明者；および
(75) 発明者／出願人（米国についてのみ）
辰巳 徹(TATSUMI, Toru)[JP/JP]
山下 篤(YAMASHITA, Atsushi)[JP/JP]
〒108-8001 東京都港区芝五丁目7番1号
日本電気株式会社内 Tokyo, (JP)
(74) 代理人
若林 忠, 外(WAKABAYASHI, Tadashi et al.)
〒107-0052 東京都港区赤坂1丁目9番20号
第16興和ビル8階 Tokyo, (JP)

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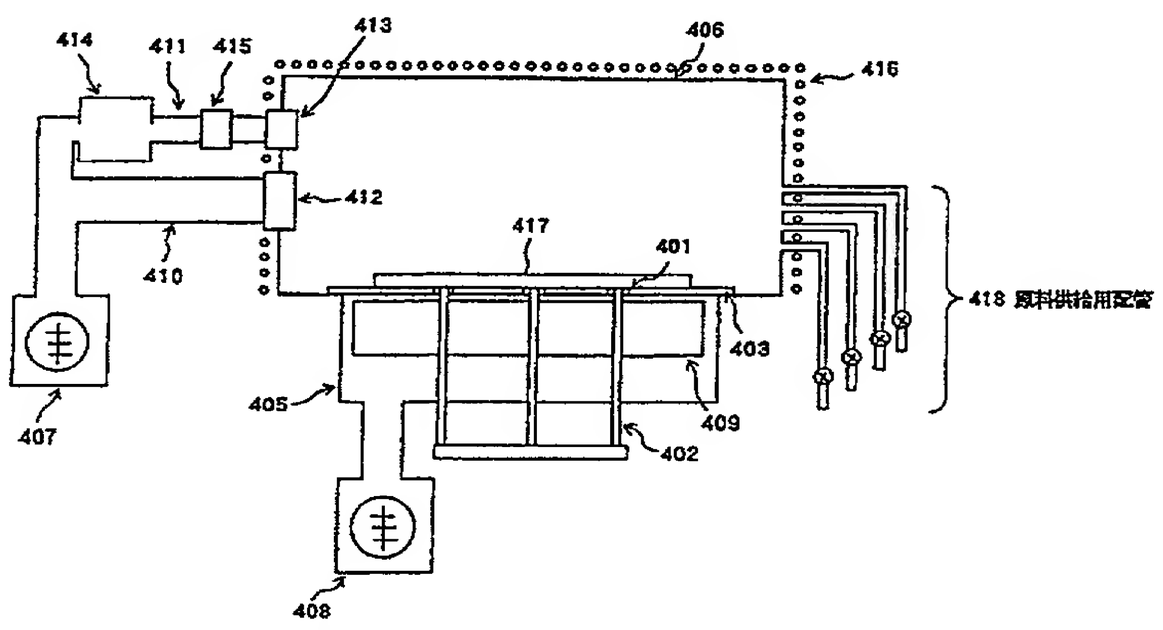
(54)Title: VAPOR GROWTH METHOD FOR METAL OXIDE DIELECTRIC FILM AND VAPOR GROWTH DEVICE FOR METAL OXIDE DIELECTRIC MATERIAL

(54)発明の名称 金属酸化物誘電体膜の気相成長方法および金属酸化物誘電体材料の気相成長装置



418 ... MATERIAL SUPPLY PIPES

(57) Abstract

A vapor growth method for a metal oxide dielectric film capable of forming on a plug a metallic oxide excellent in orientation and crystallinity at low temperature, comprising introducing an organic metal material gas and an oxidizing gas into a vacuum container from separate inlets while a substrate disposed in the vacuum container being heated and forming a film with a total pressure within the vacuum container kept at not higher than $1x10^{-2}$Torr; the method further comprising, when forming a metal oxide dielectric film having a Perovskite type crystal structure, using different film forming conditions for a first film forming condition for forming an initial nucleus or an initial layer and a second film forming condition for growing a film of a Perovskite type crystal structure on the formed initial nucleus and selecting an optimum one of the conditions for film forming; and a vapor growth device for implementing the above vapor growth methods.

ABSTRACT

The present invention relates to a vapor phase growth method of a metal oxide dielectric film and capable of forming a metal oxide with excellent in both orientation and crystallinity on a plug at a low temperature and carries out film formation by introducing the organometal gases and an oxidizing gas into a vacuum chamber through separate introduction inlets while heating the substrate set in the vacuum chamber at 1×10^{-2} Torr or lower of the total pressure of the vacuum chamber. Further, the present invention is for carrying out film formation of a metal oxide dielectric film with a perovskite type crystal structure by changing film formation conditions and properly selecting optimum conditions for first film formation conditions for initial nuclei or layer formation and second film formation conditions for film formation of the perovskite type crystal structure further on the formed initial nuclei. The present invention further relates to a vapor phase growth apparatus to be employed for the vapor phase growth methods.

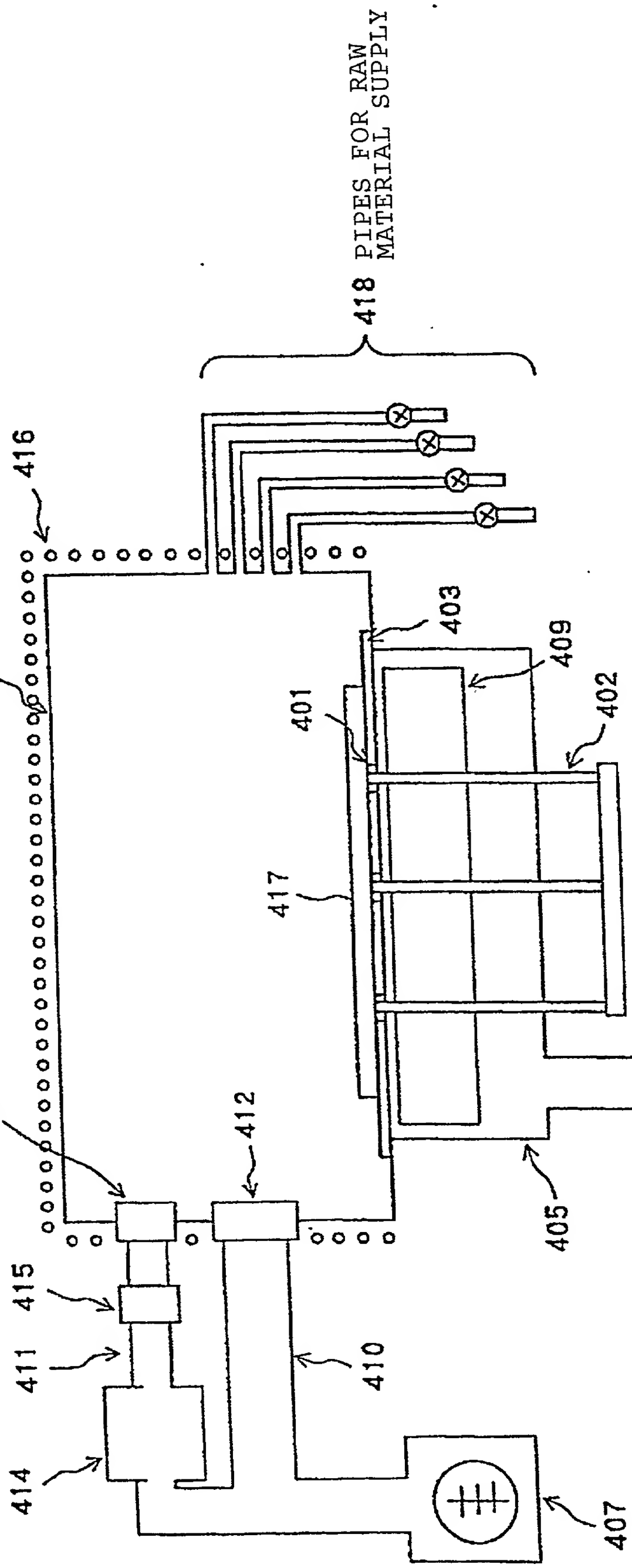

418 PIPES FOR RAW MATERIAL SUPPLY
416
406
413
412
415
411
414
403
409
401
402
417
405
410
408
407

Fig. 1

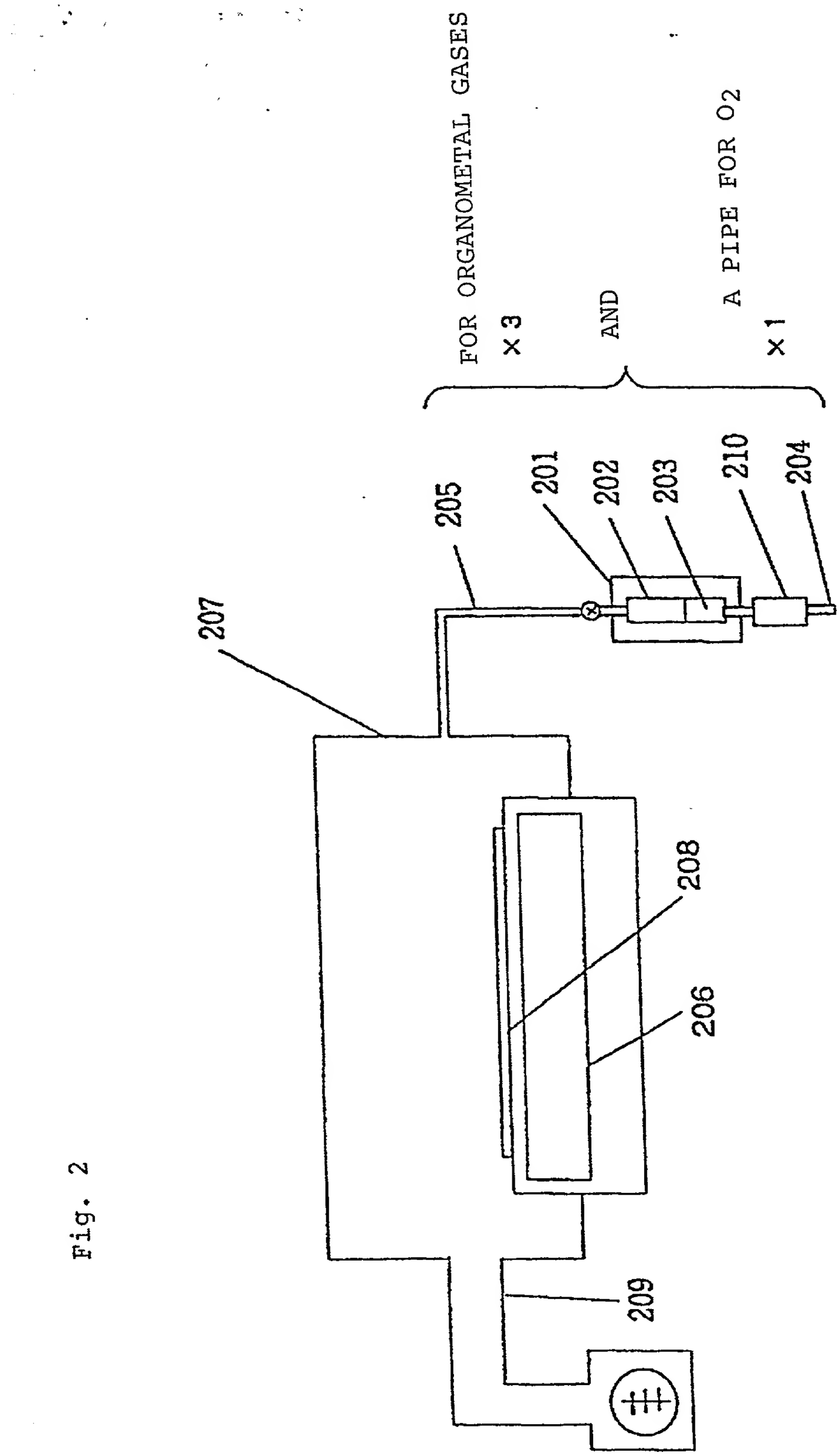


Fig. 2

Fig. 3

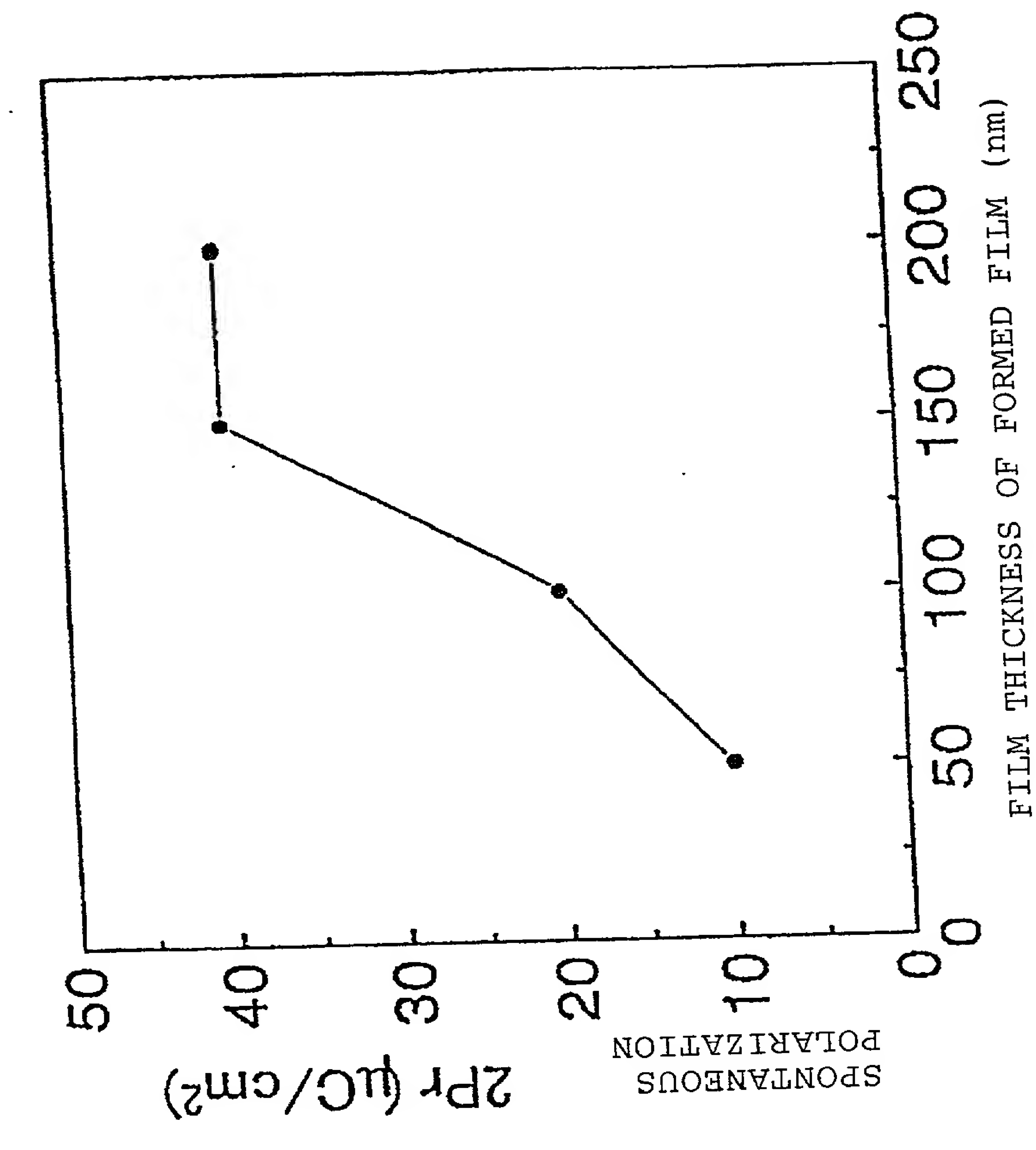

SPONTANEOUS POLARIZATION
2Pr (µC/cm2)
0
10
20
30
40
50
0
50
100
150
200
250
FILM THICKNESS OF FORMED FILM (nm)

Fig. 4

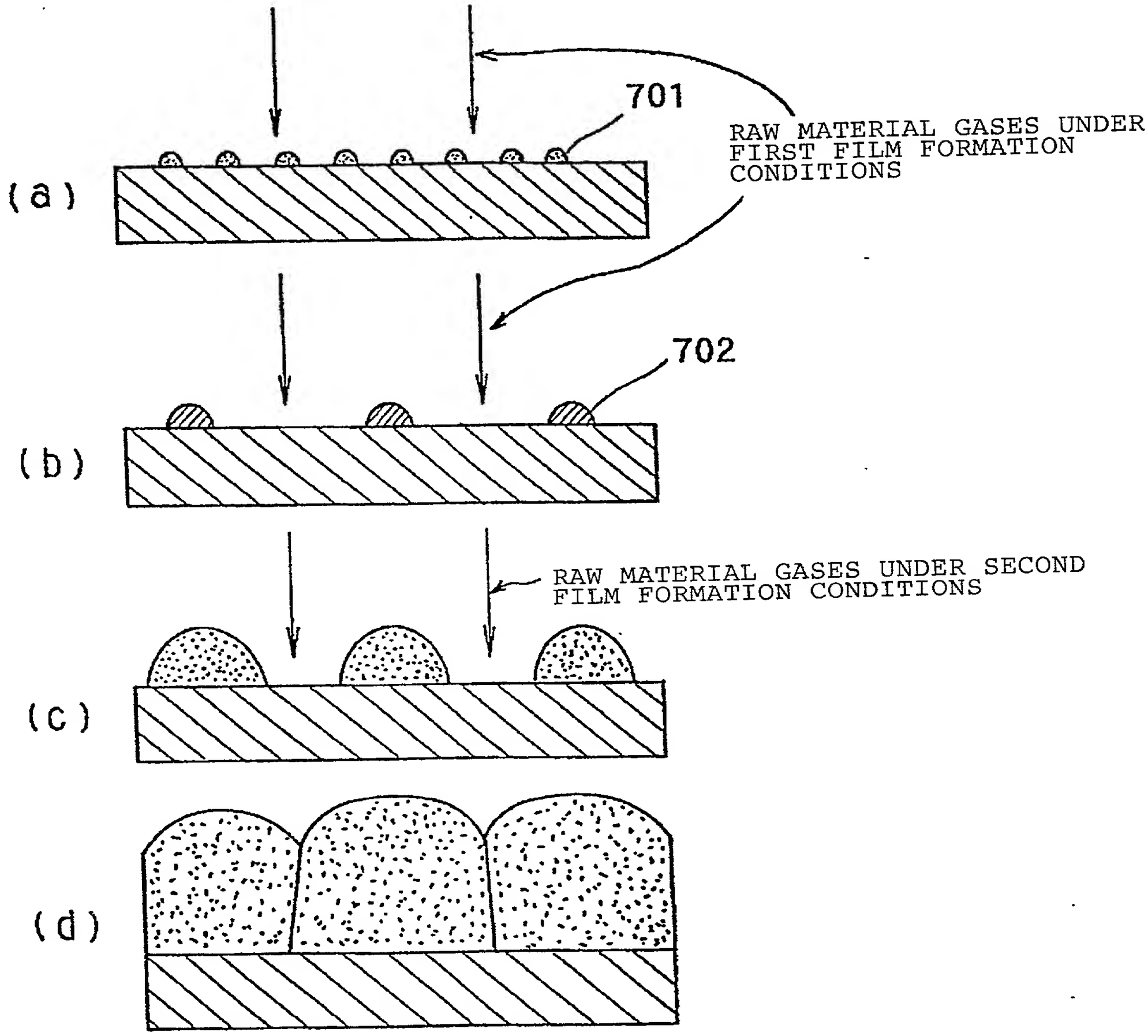
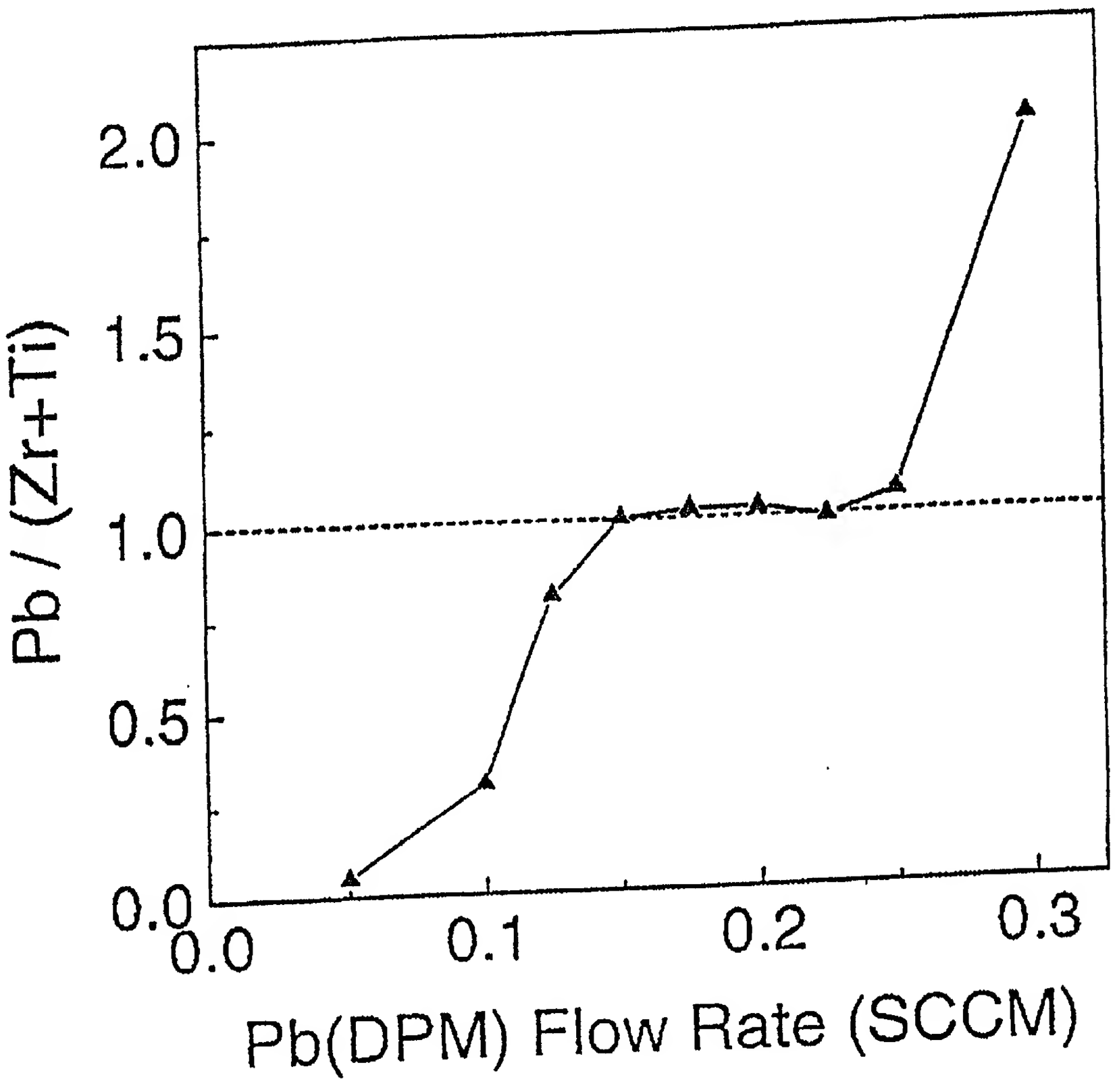


Fig. 5



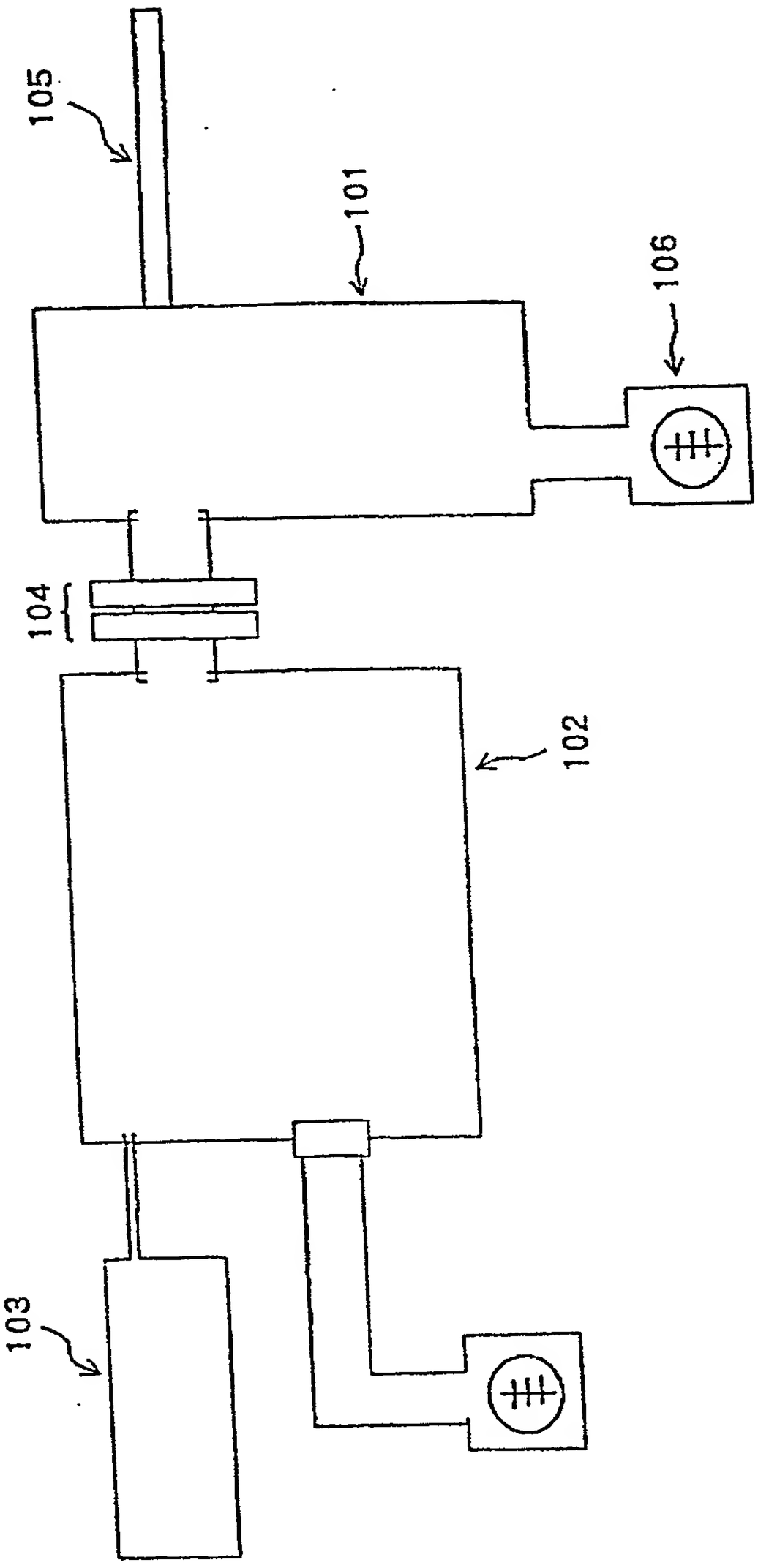


Fig. 6

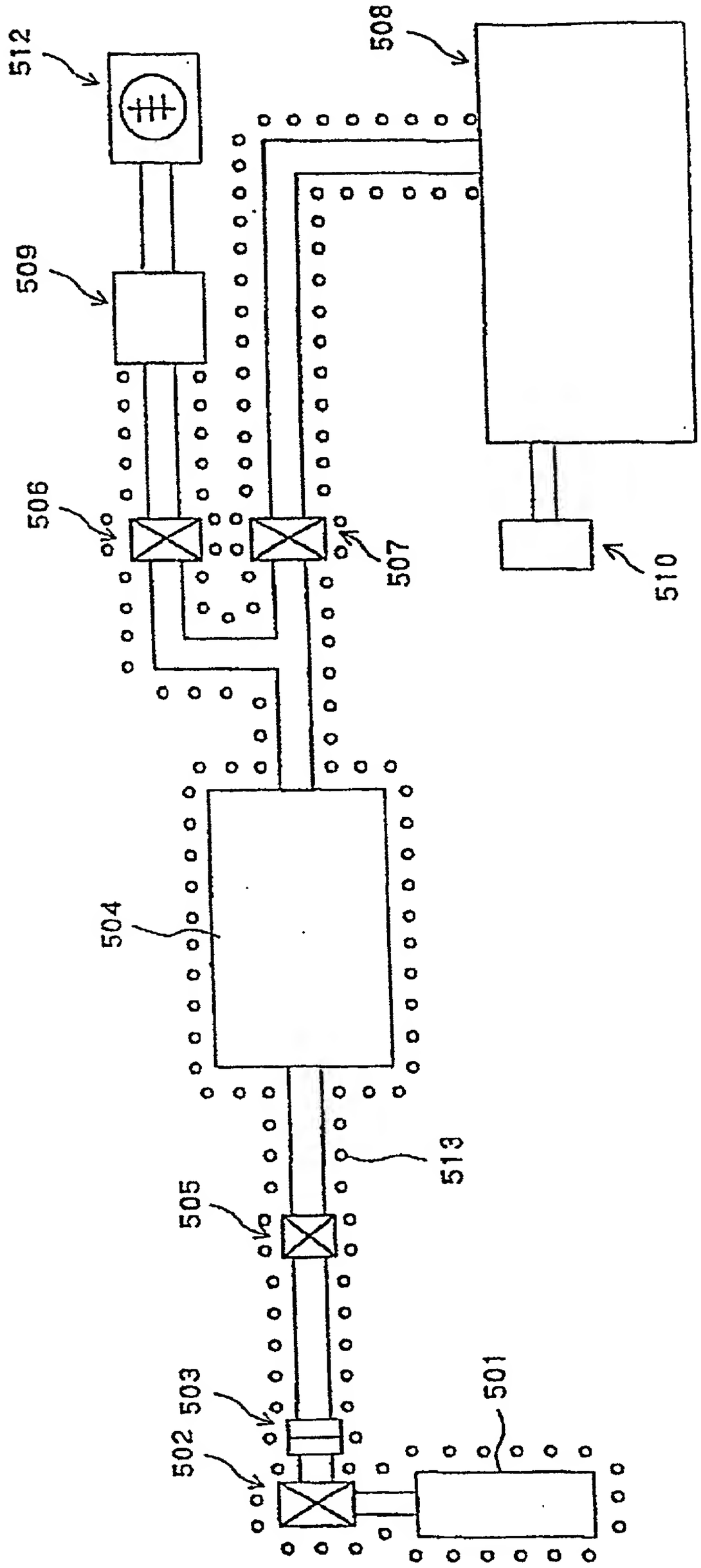
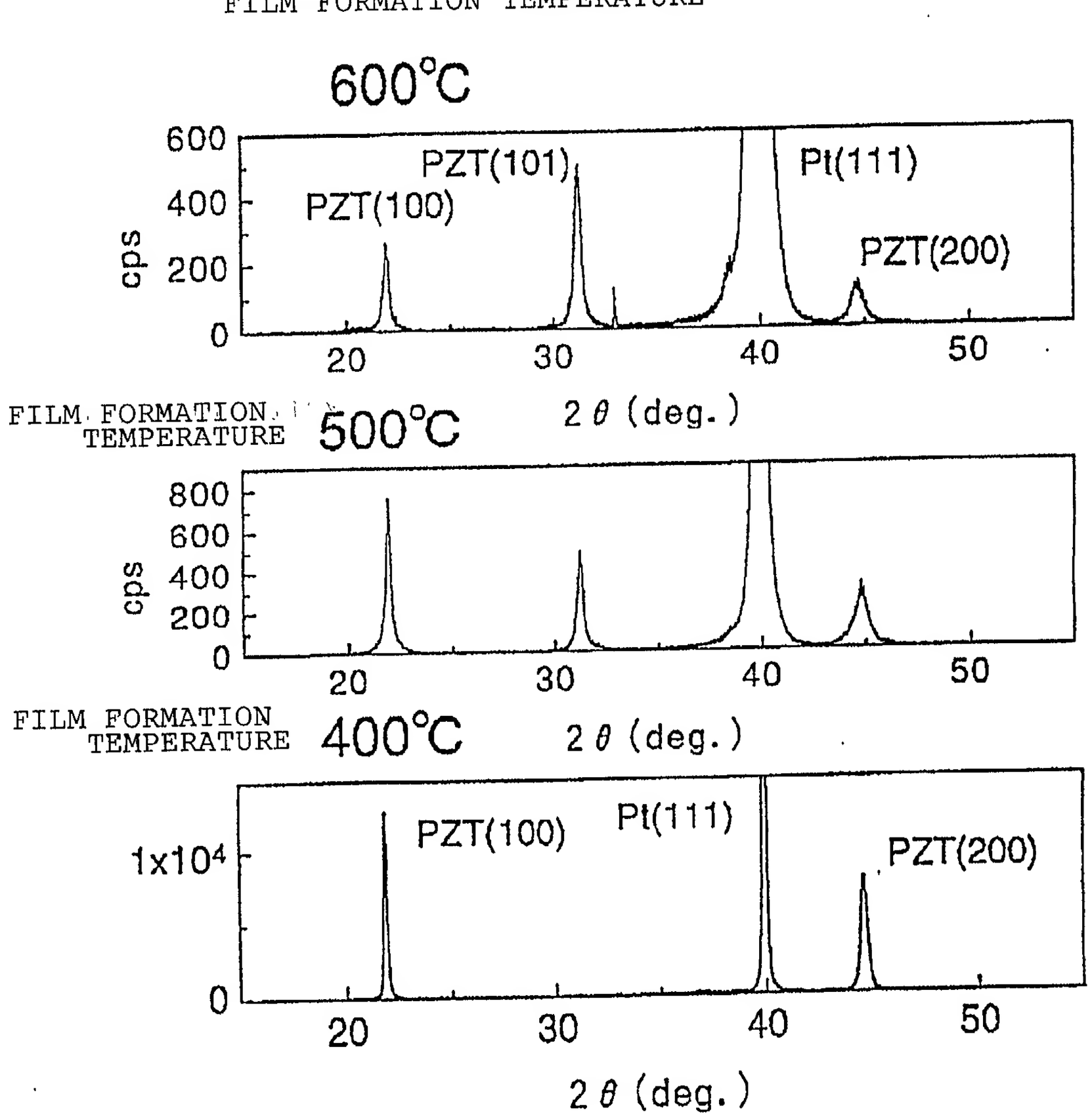


Fig. 7

Fig. 8


FILM FORMATION TEMPERATURE
600°C
600
400
200
0
cps
PZT(100)
PZT(101)
Pt(111)
PZT(200)
20
30
40
50
2θ (deg.)
FILM FORMATION TEMPERATURE
500°C
800
600
400
200
0
cps
20
30
40
50
2θ (deg.)
FILM FORMATION TEMPERATURE
400°C
1x10⁴
0
PZT(100)
Pt(111)
PZT(200)
20
30
40
50
2θ (deg.)

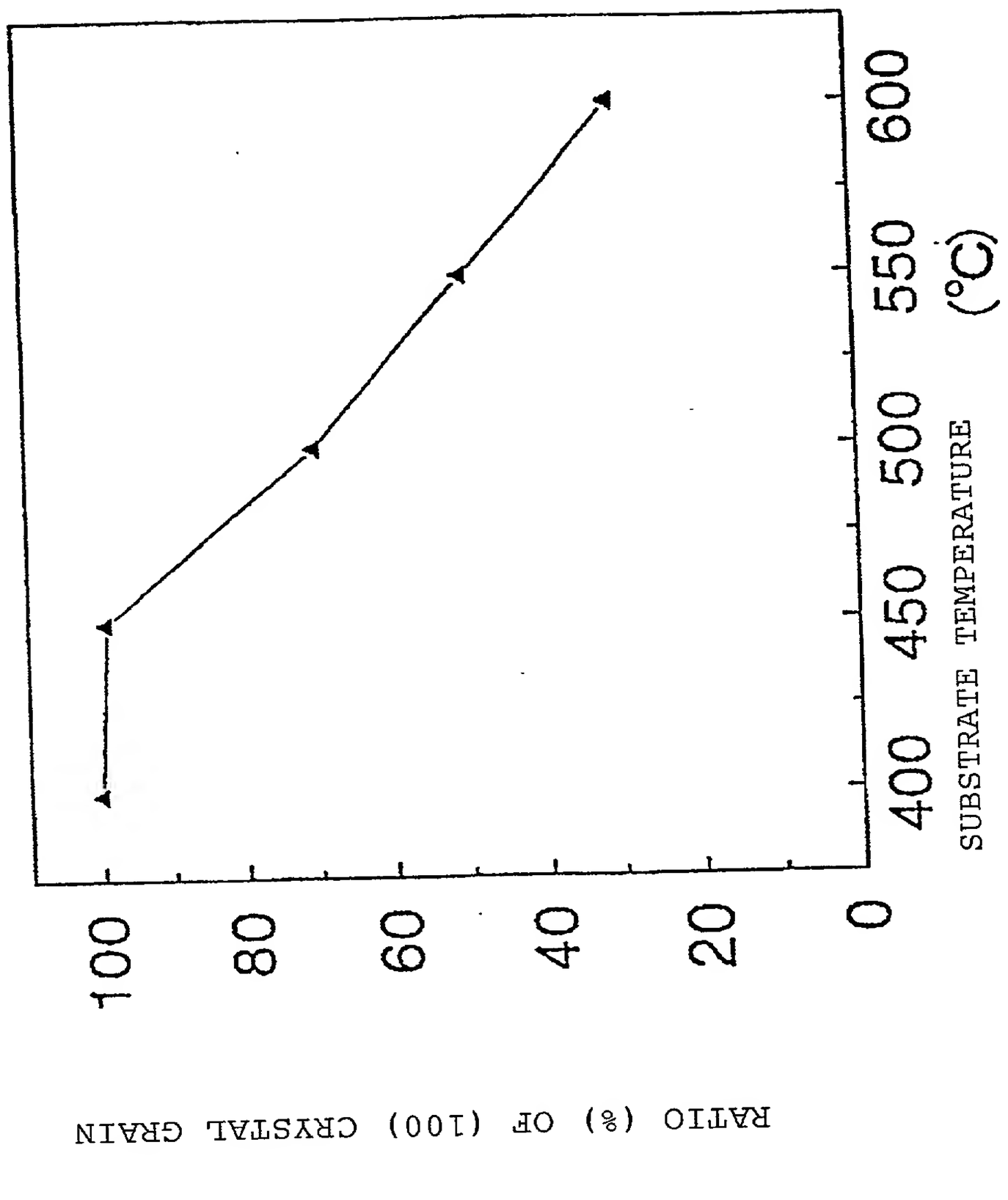

100
80
60
40
20
0
400
450
500
550
600
SUBSTRATE TEMPERATURE (°C)
RATIO (%) OF (100) CRYSTAL GRAIN

Fig. 9

Fig. 10

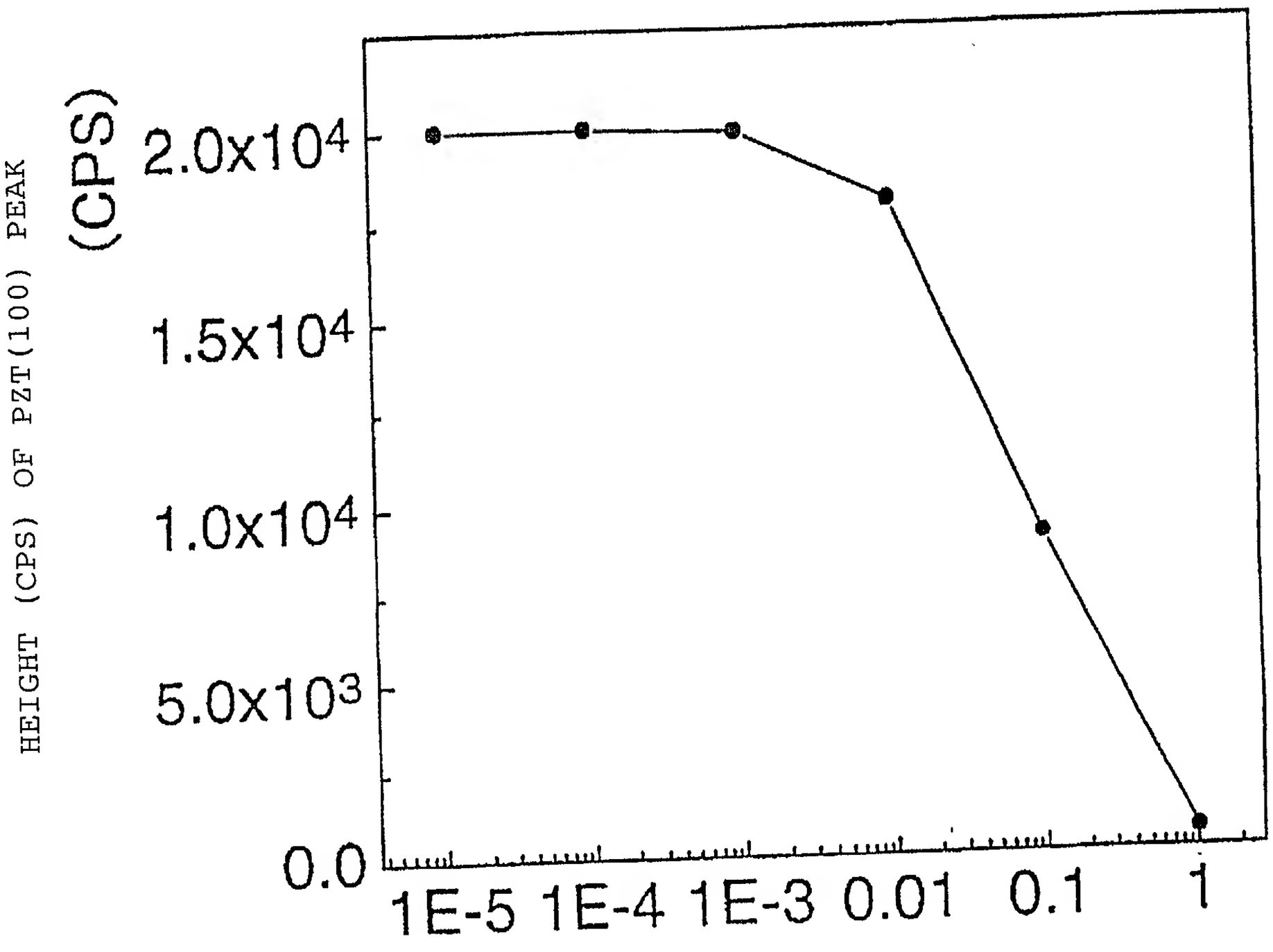
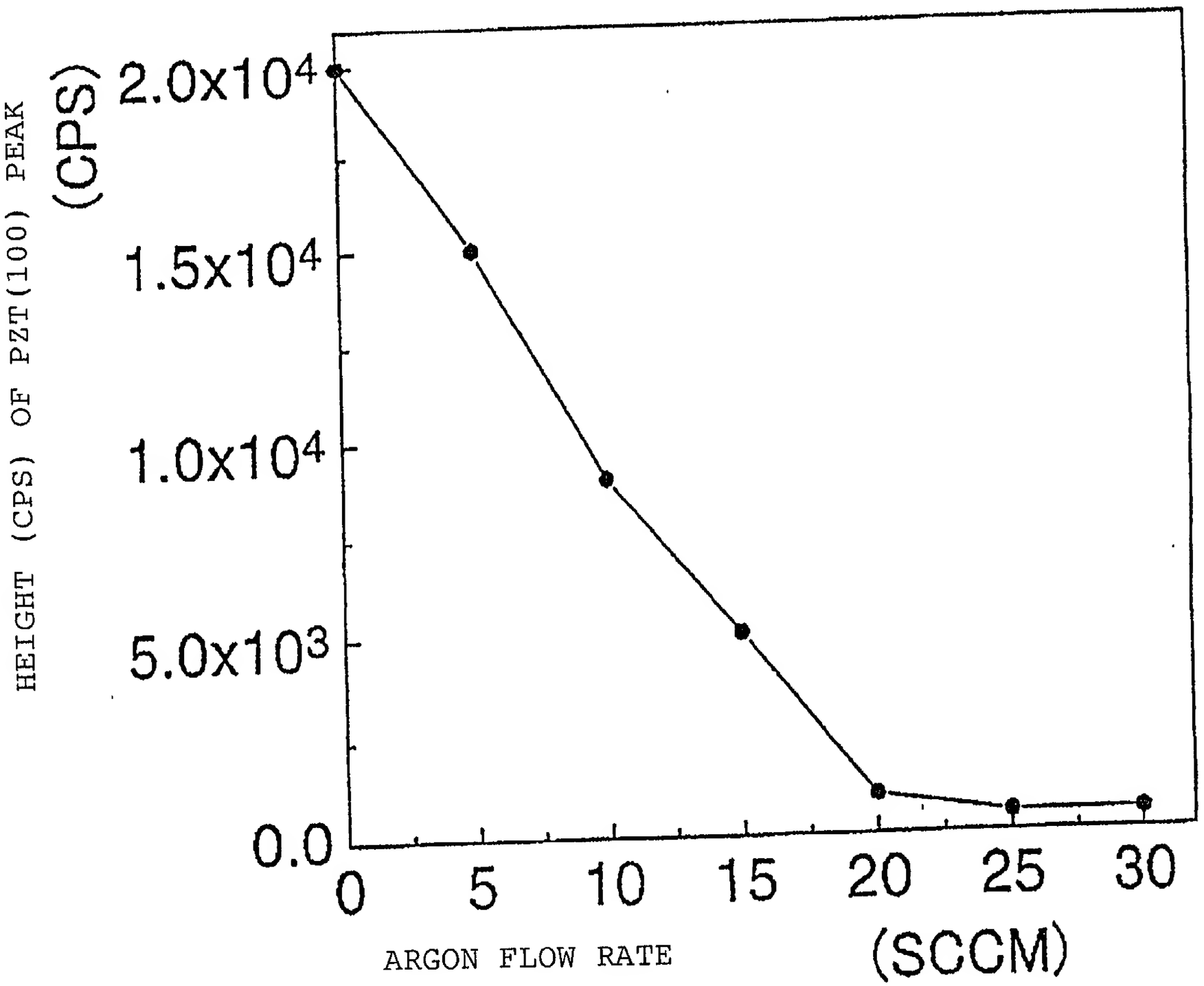


Fig. 11


HEIGHT (CPS) OF PZT(100) PEAK
(CPS)
2.0x10⁴
1.5x10⁴
1.0x10⁴
5.0x10³
0.0
0
5
10
15
20
25
30
ARGON FLOW RATE
(SCCM)

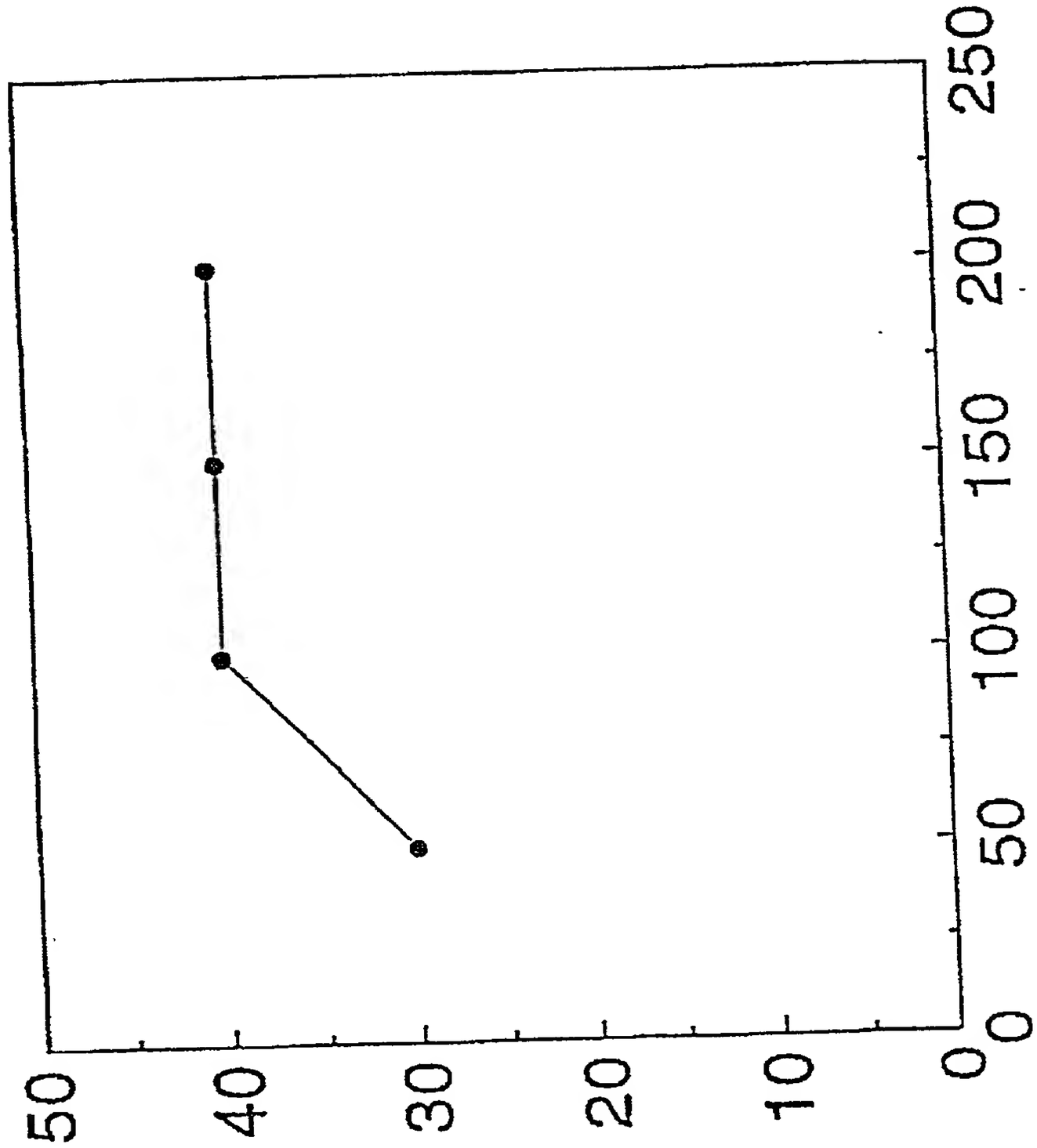
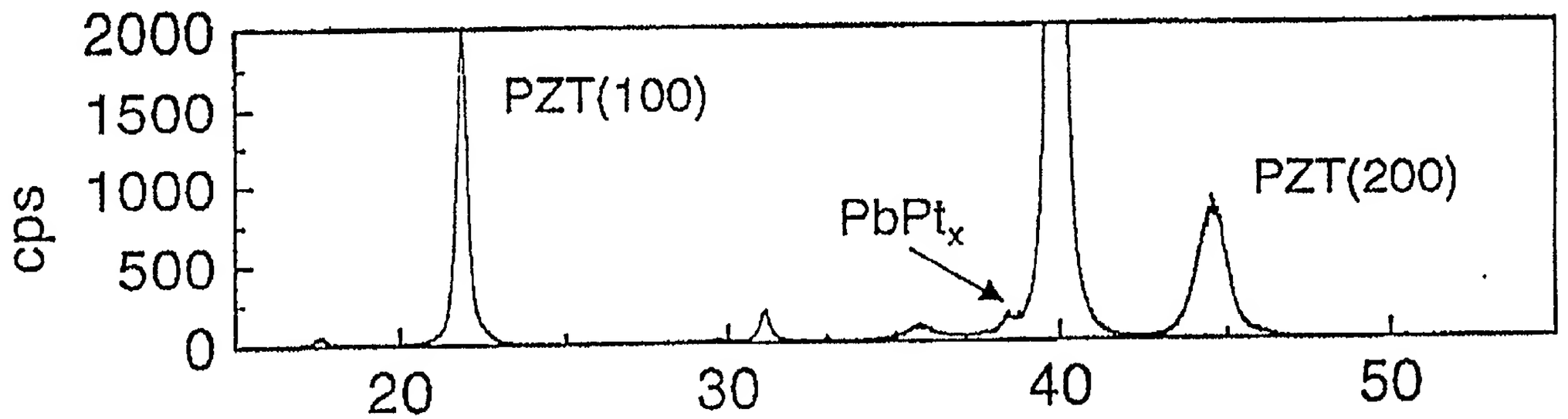

50
40
30
20
10
0
0
50
100
150
200
250
FILM THICKNESS OF FORMED FILM (nm)
SPONTANEOUS POLARIZATION
2Pr (μC/cm2)

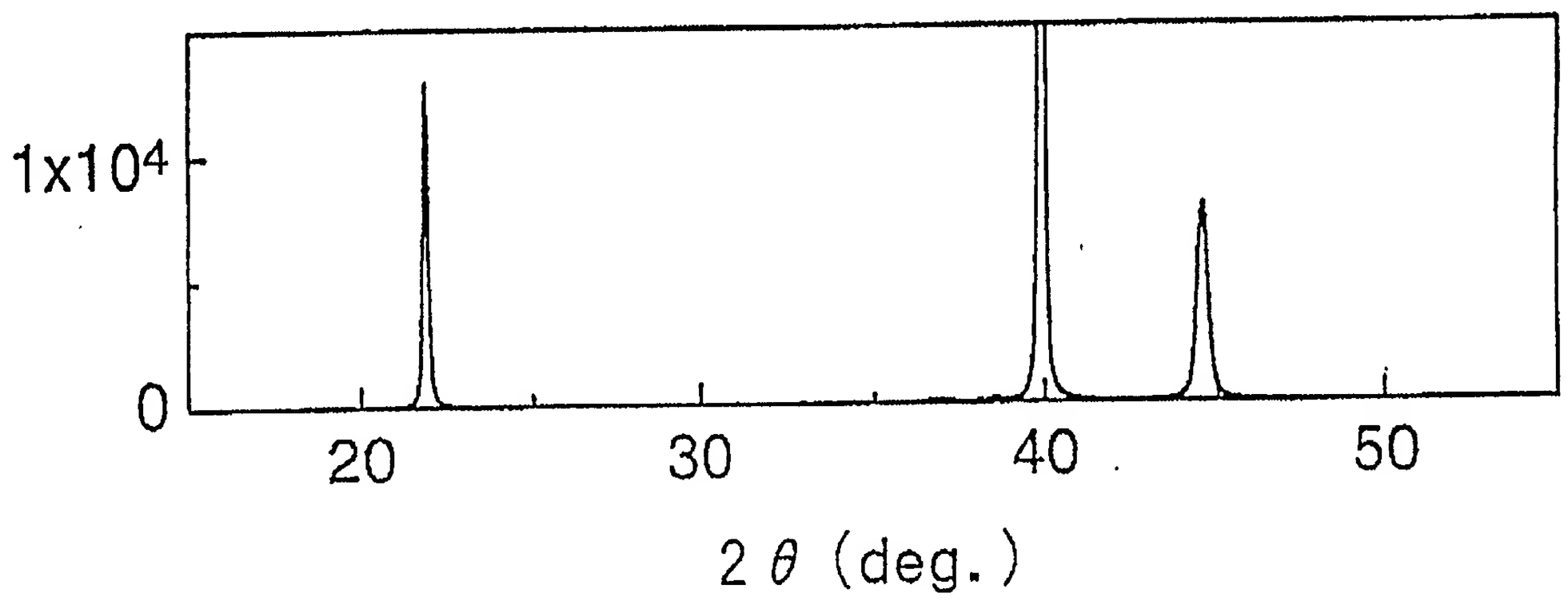
Fig. 12

Fig. 13

IN THE CASE OF USING OXYGEN AS OXIDIZING AGENT



IN THE CASE OF USING NITROGEN DIOXIDE AS OXIDIZING AGENT



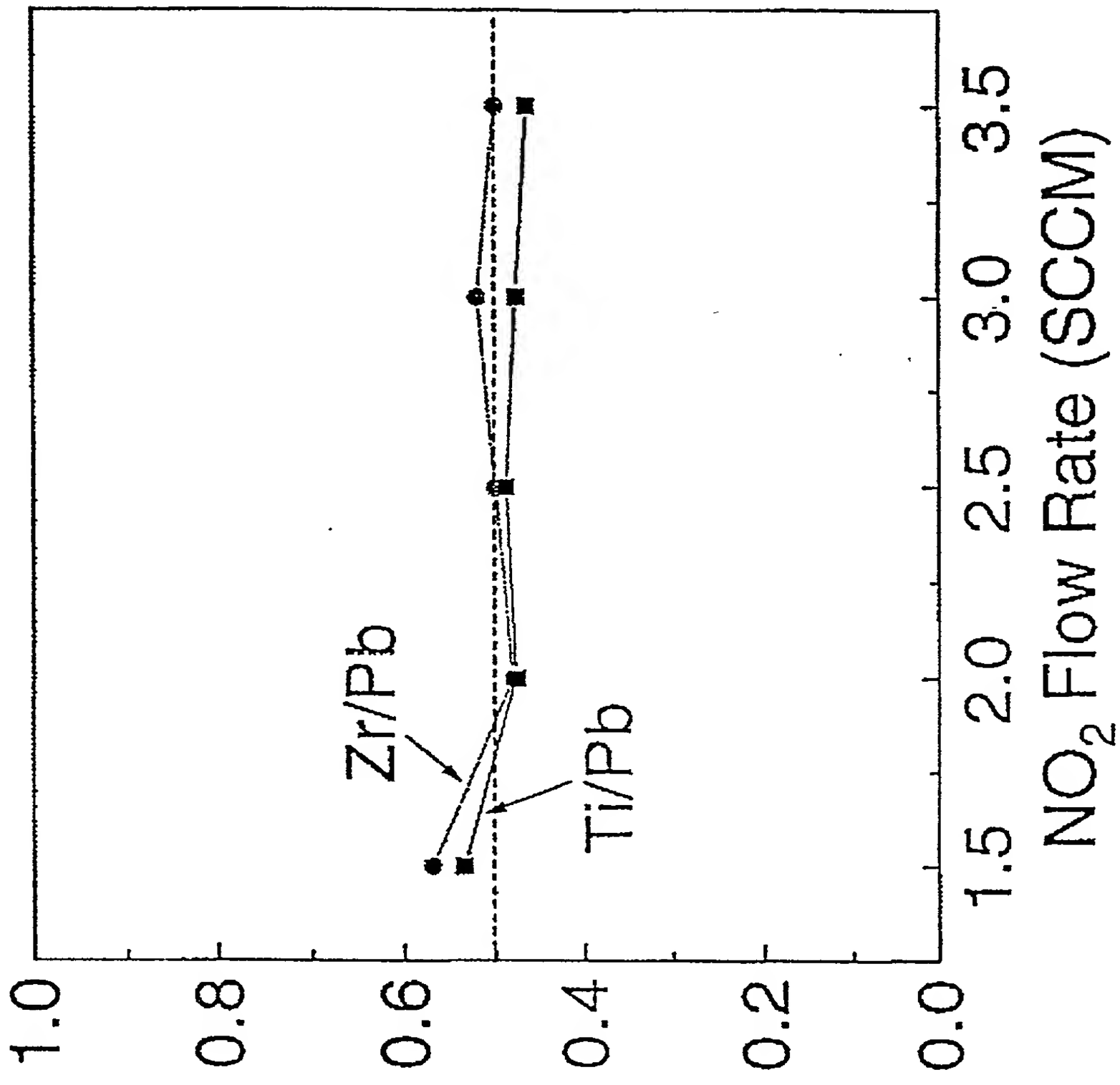

Zr/Pb
Ti/Pb
1.0
0.8
0.6
0.4
0.2
0.0
1.5
2.0
2.5
3.0
3.5
NO_2 Flow Rate (SCCM)
Concentration Ratio

Fig. 14

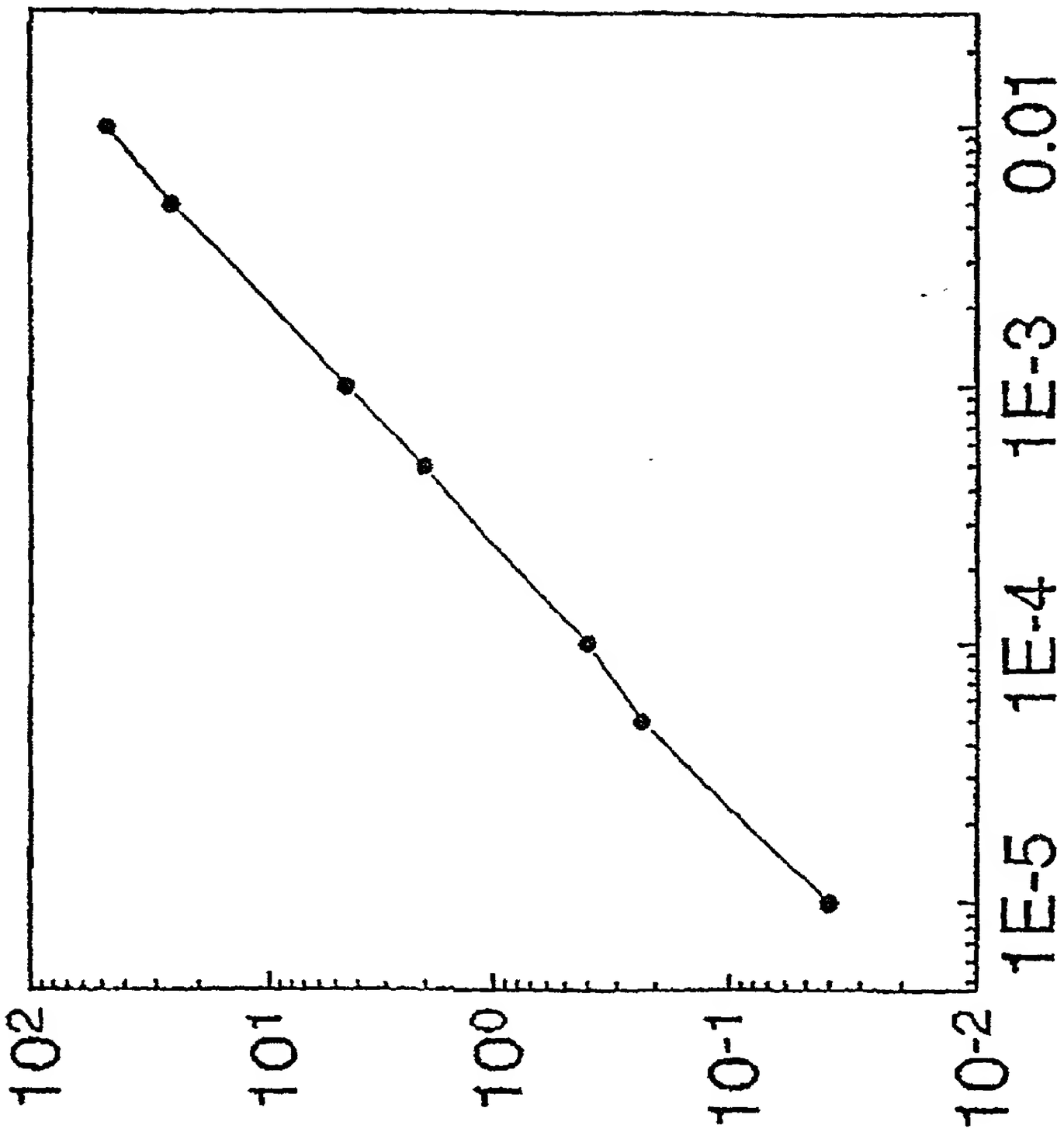

FILM FORMATION RATE (nm/min)
10-2
10-1
100
101
102
1E-5
1E-4
1E-3
0.01
PRESSURE (Torr) AT THE TIME OF FILM FORMATION

Fig. 15

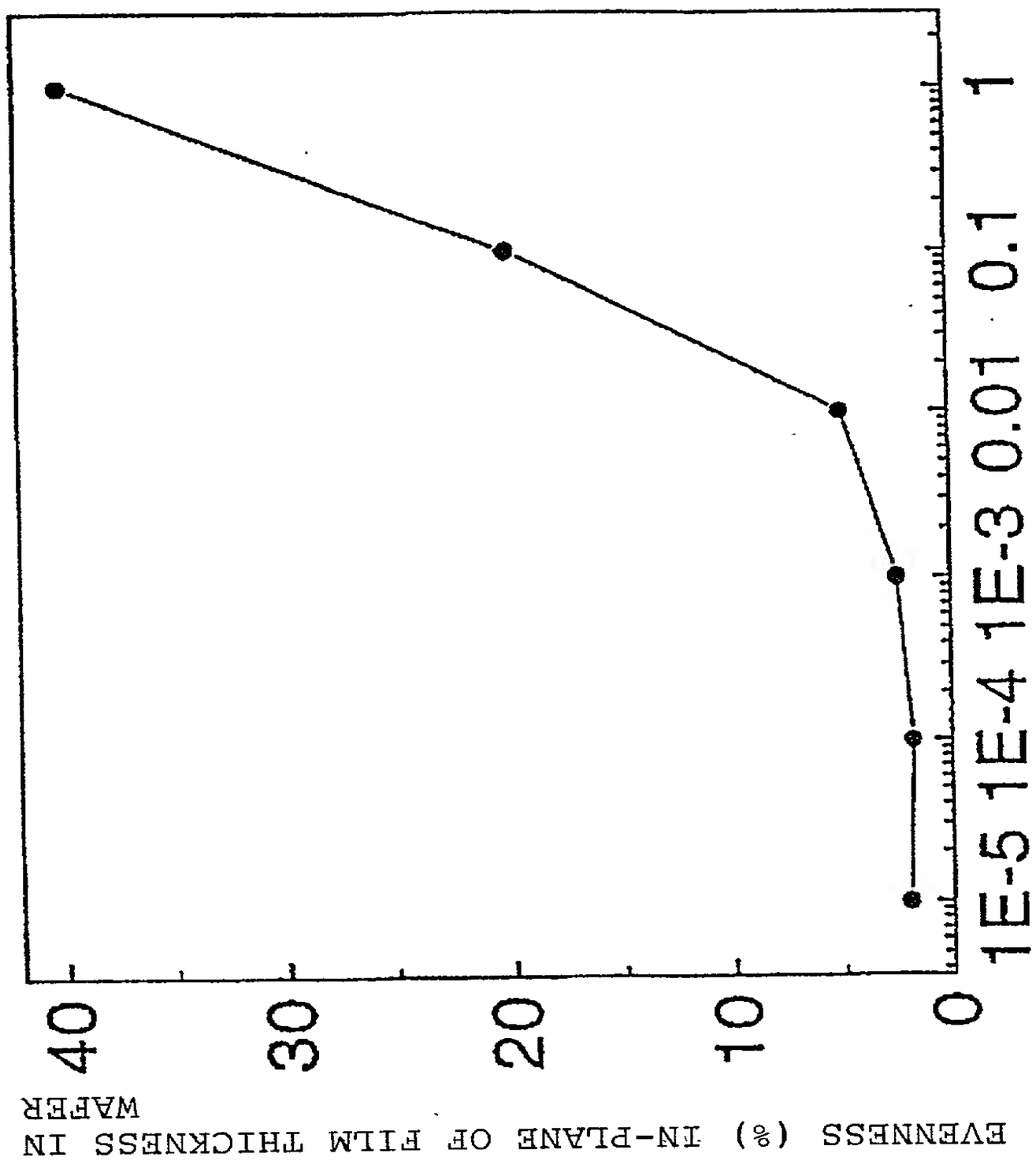


Fig. 16

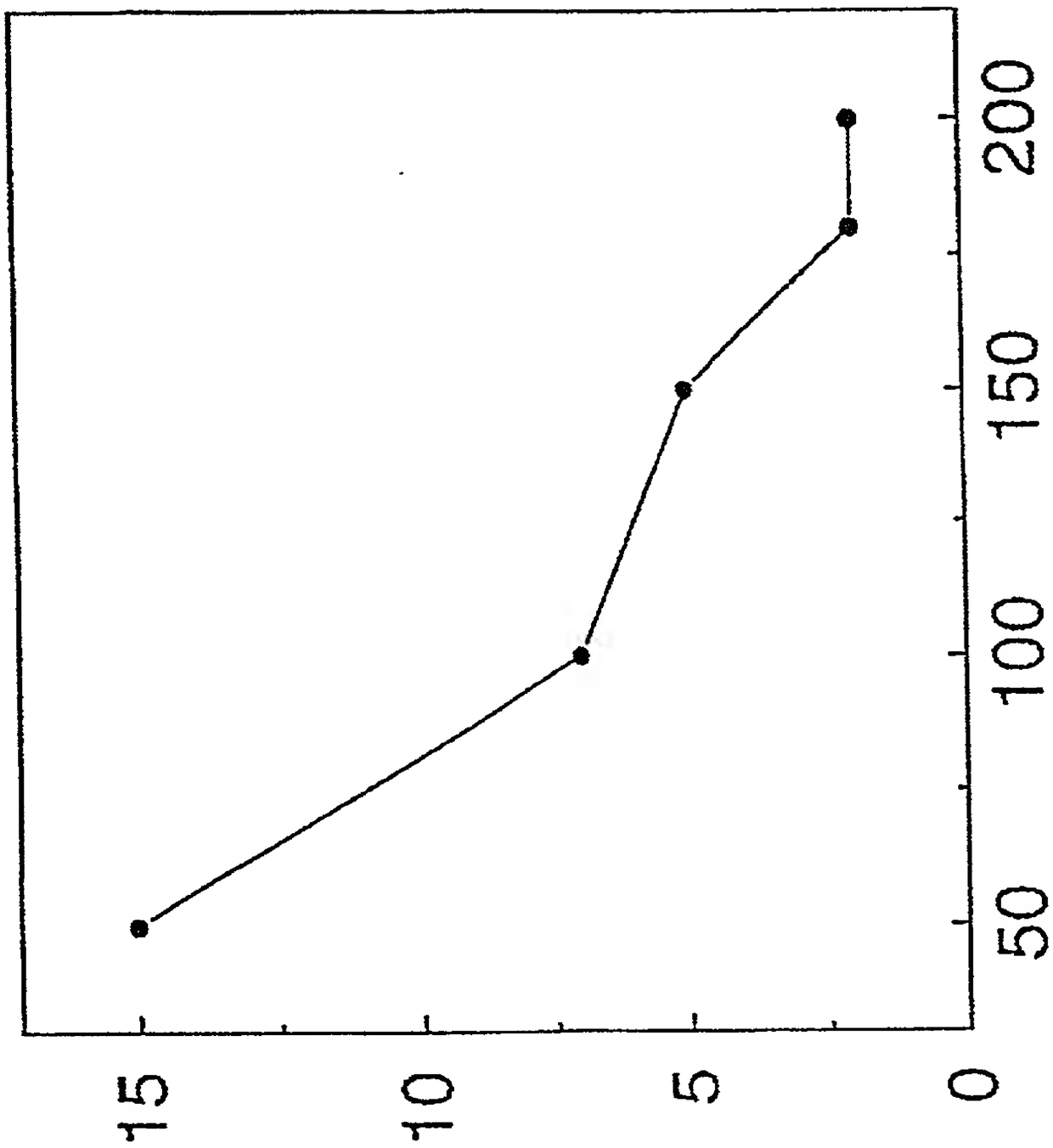

0
5
10
15
50
100
150
200
EVENNESS (%) IN-PLANE OF FILM THICKNESS IN WAFER
INNER WALL TEMPERATURE (°C) OF VACUUM CHAMBER

Fig. 17

Fig. 18

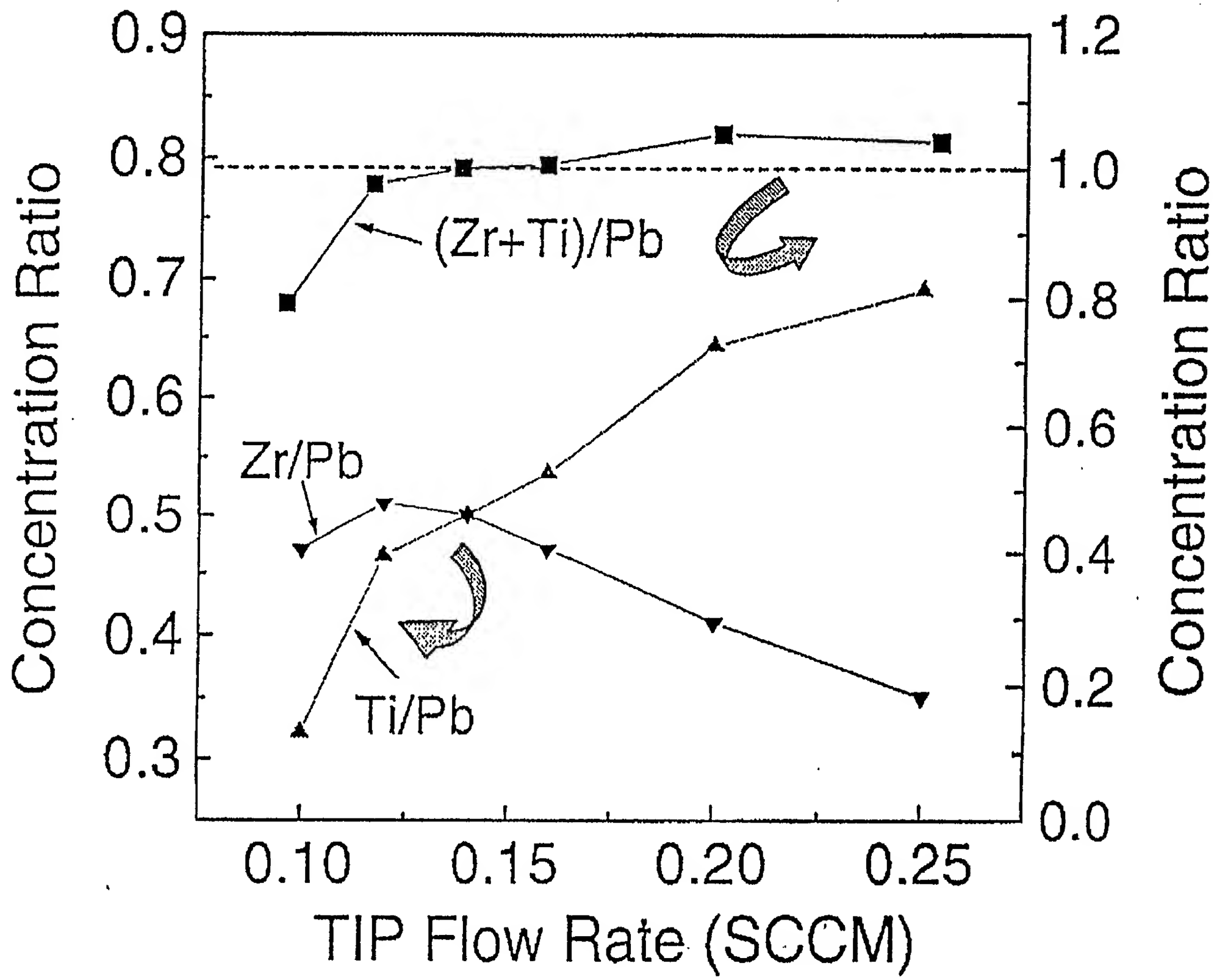


Fig. 19

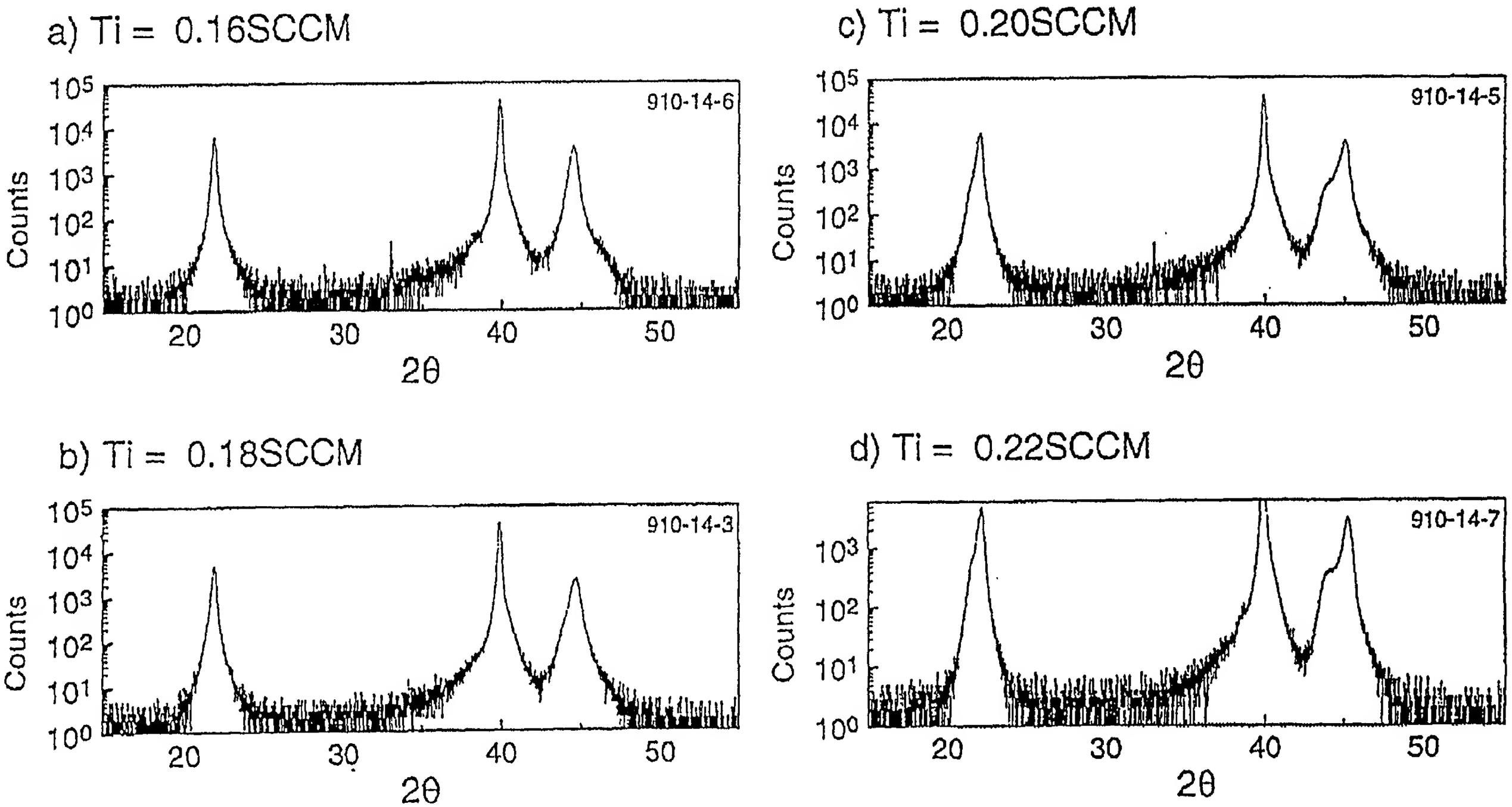
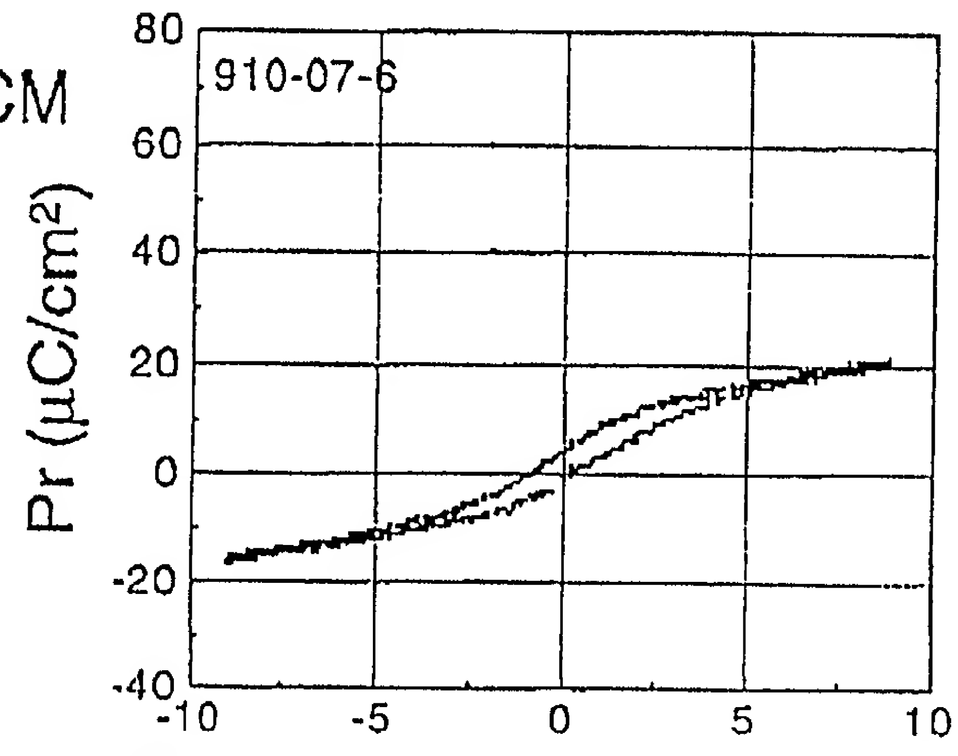
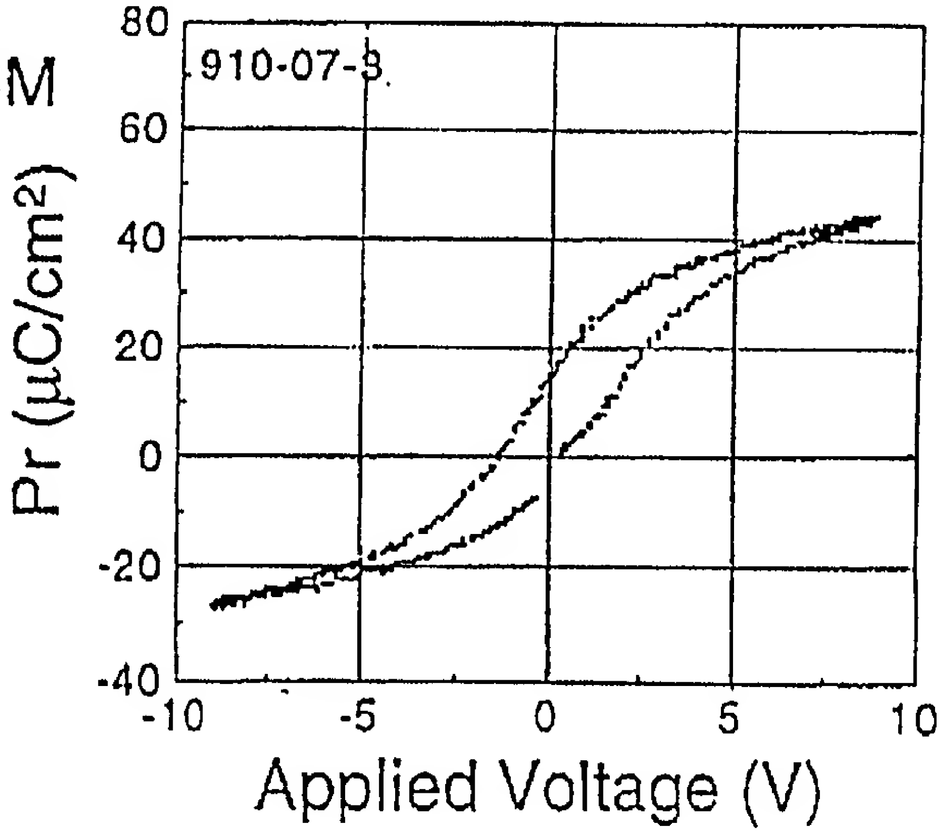


Fig. 20

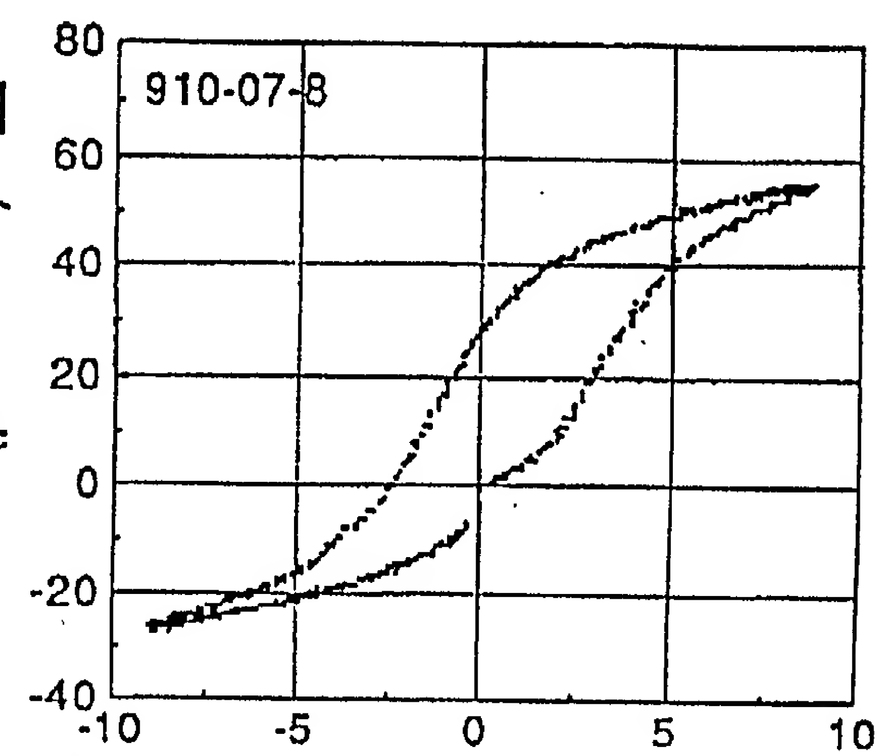
a) Ti = 0.14SCCM



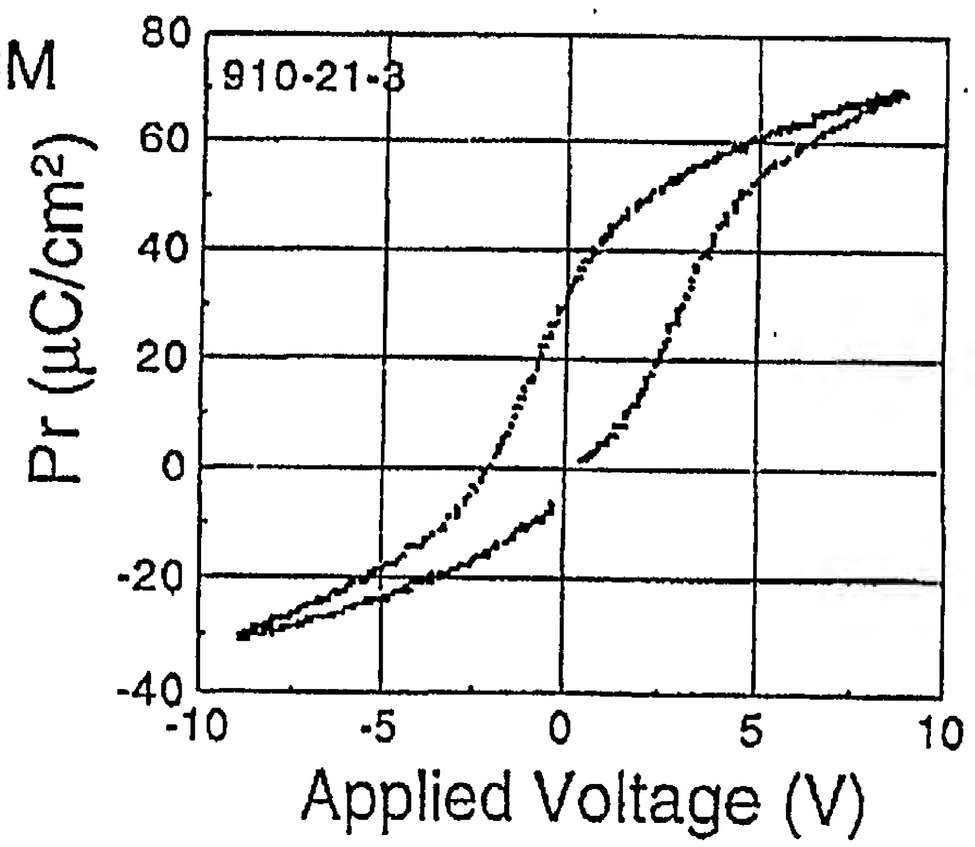
b) Ti = 0.16SCCM



c) Ti = 0.18SCCM



d) Ti = 0.2SCCM



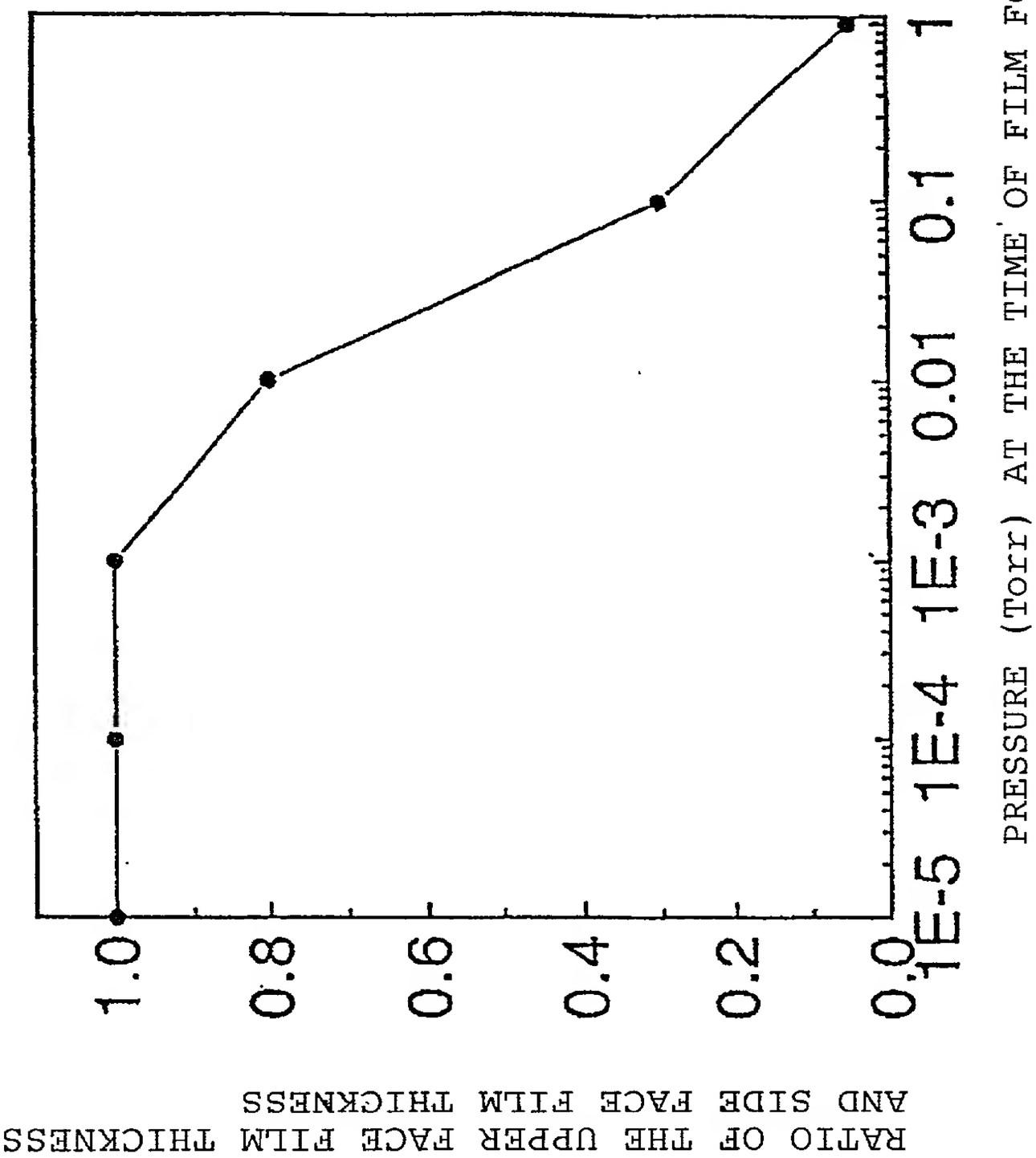

RATIO OF THE UPPER FACE FILM THICKNESS AND SIDE FACE FILM THICKNESS
1.0
0.8
0.6
0.4
0.2
0.0
1E-5
1E-4
1E-3
0.01
0.1
1
PRESSURE (Torr) AT THE TIME OF FILM FORMATION

Fig. 21

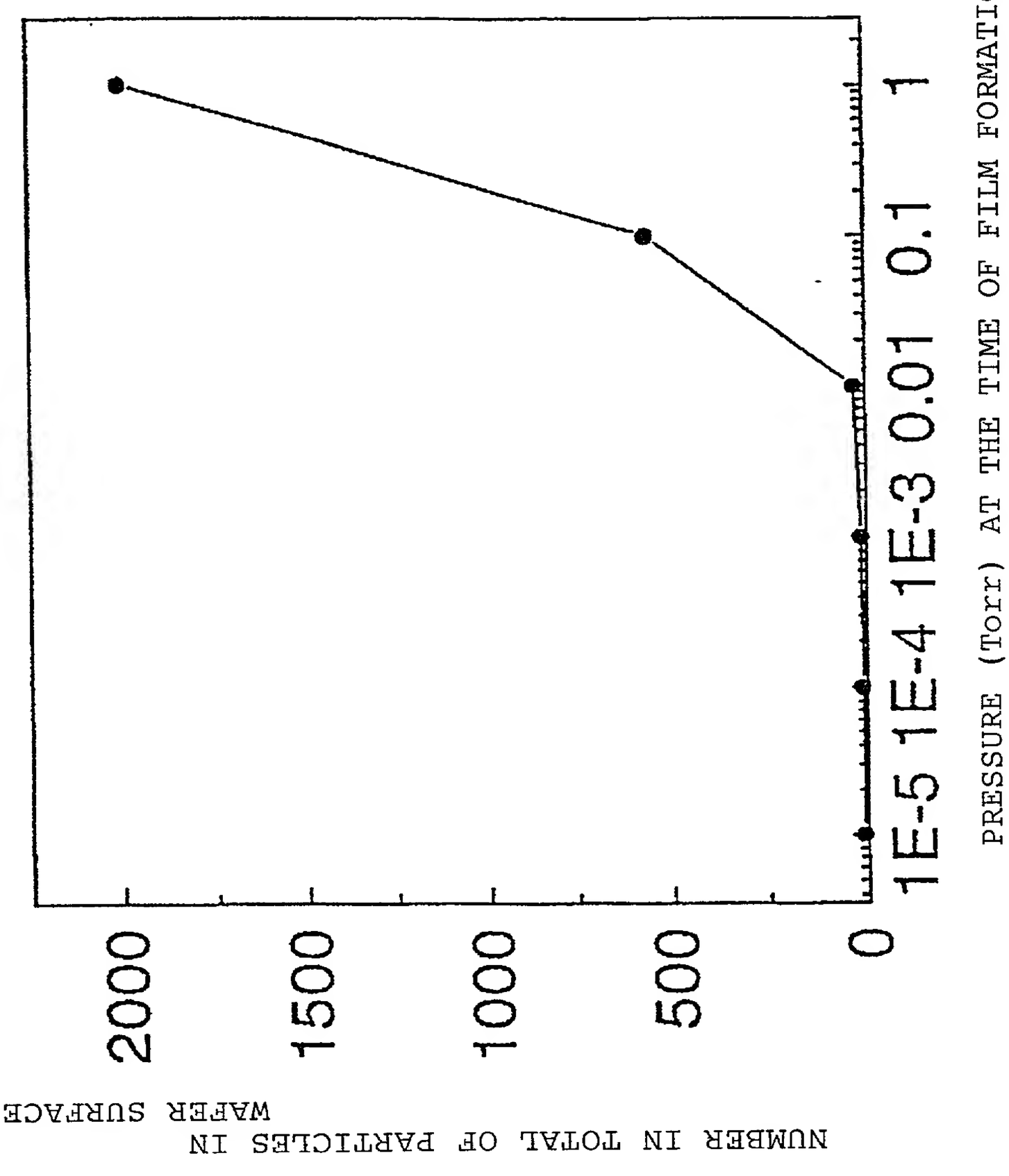

2000
1500
1000
500
0
1E-5 1E-4 1E-3 0.01 0.1 1
NUMBER IN TOTAL OF PARTICLES IN WAFER SURFACE
PRESSURE (Torr) AT THE TIME OF FILM FORMATION

Fig. 22

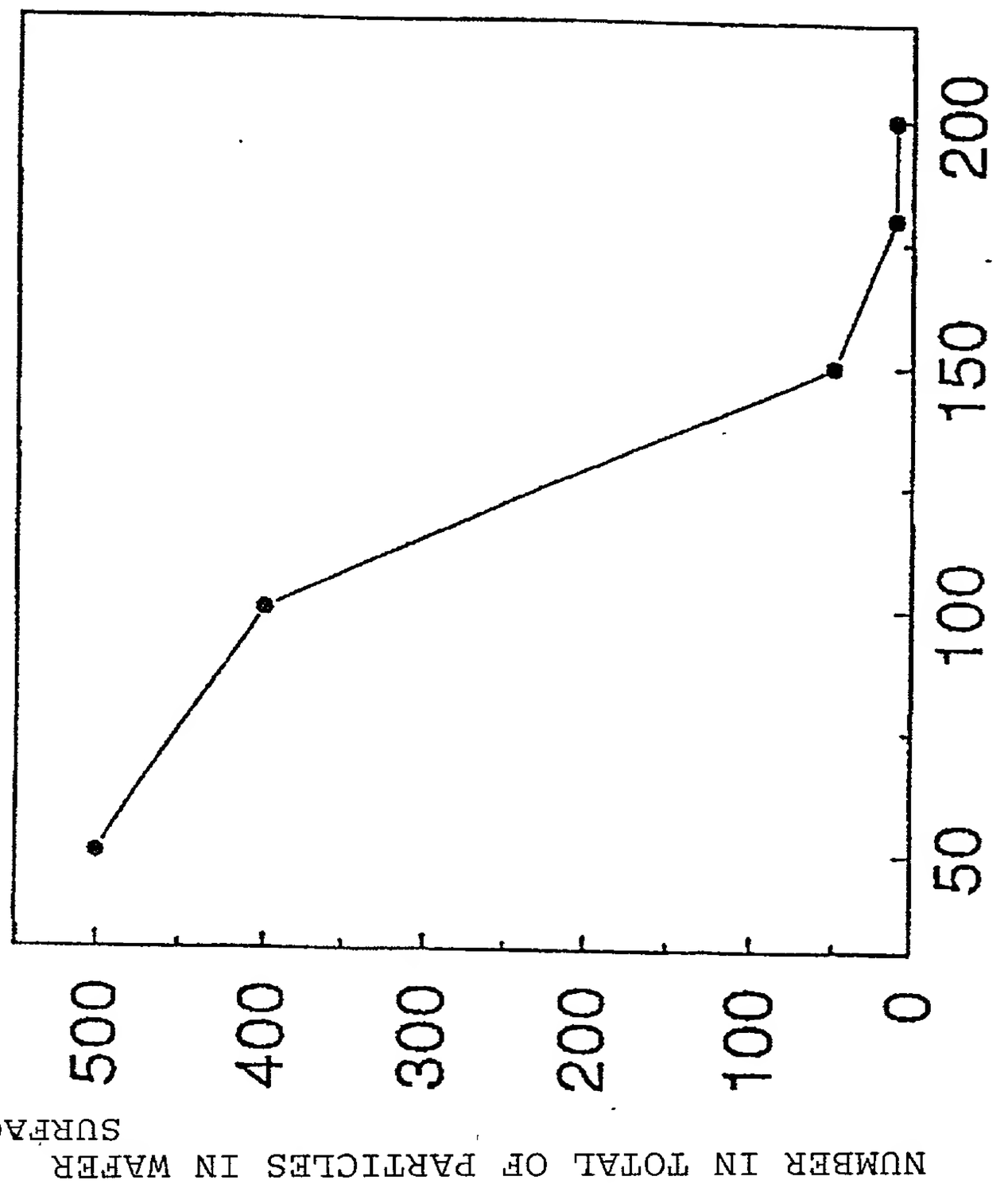
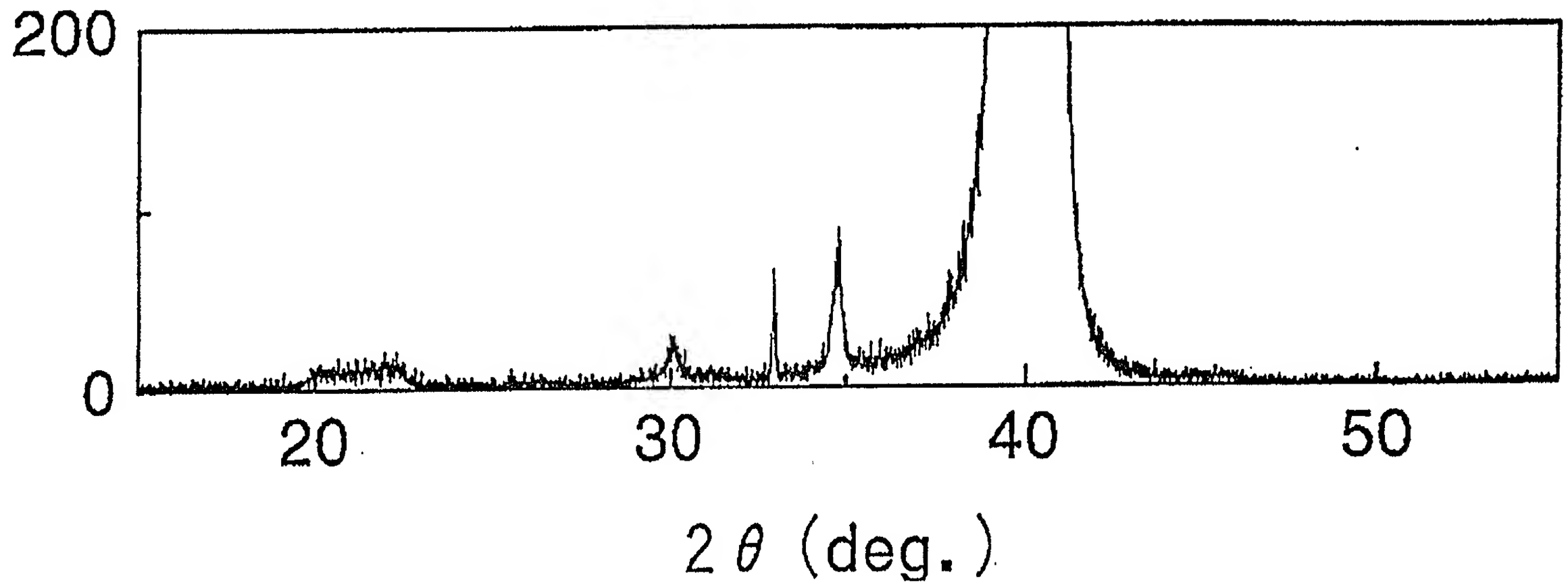

NUMBER IN TOTAL OF PARTICLES IN WAFER
SURFACE
500
400
300
200
100
0
50
100
150
200
INNER WALL TEMPERATURE (°C) OF VACUUM CHAMBER

Fig. 23

Fig. 24



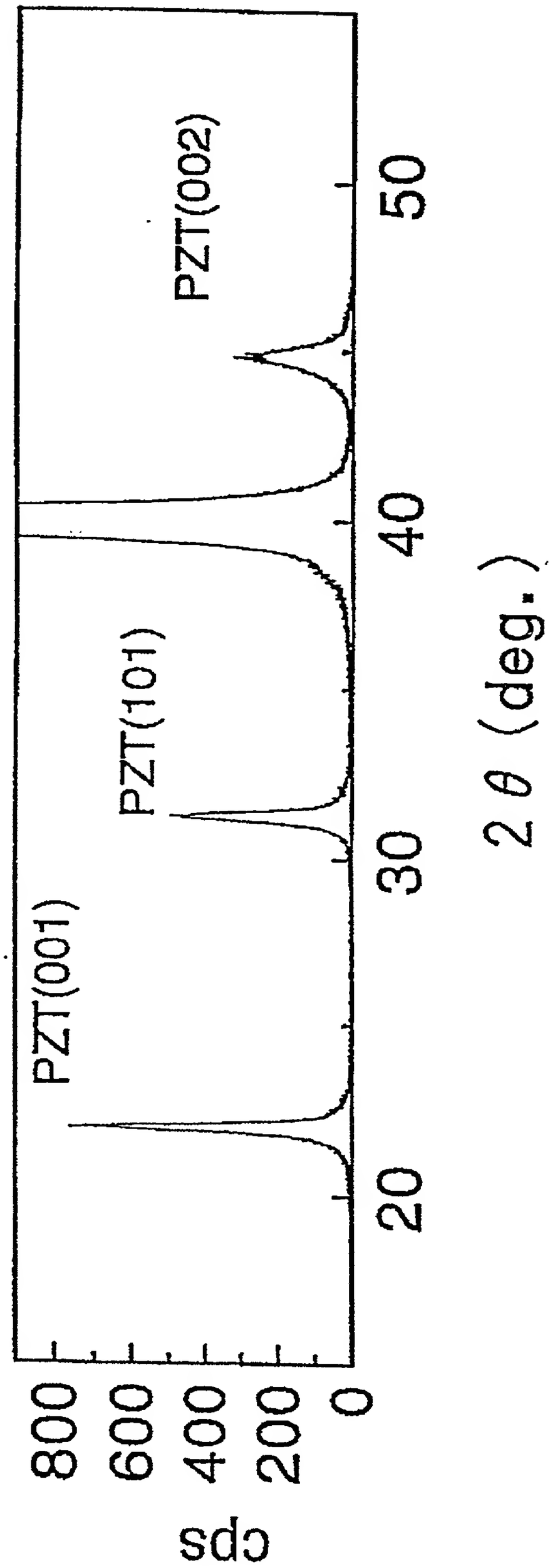
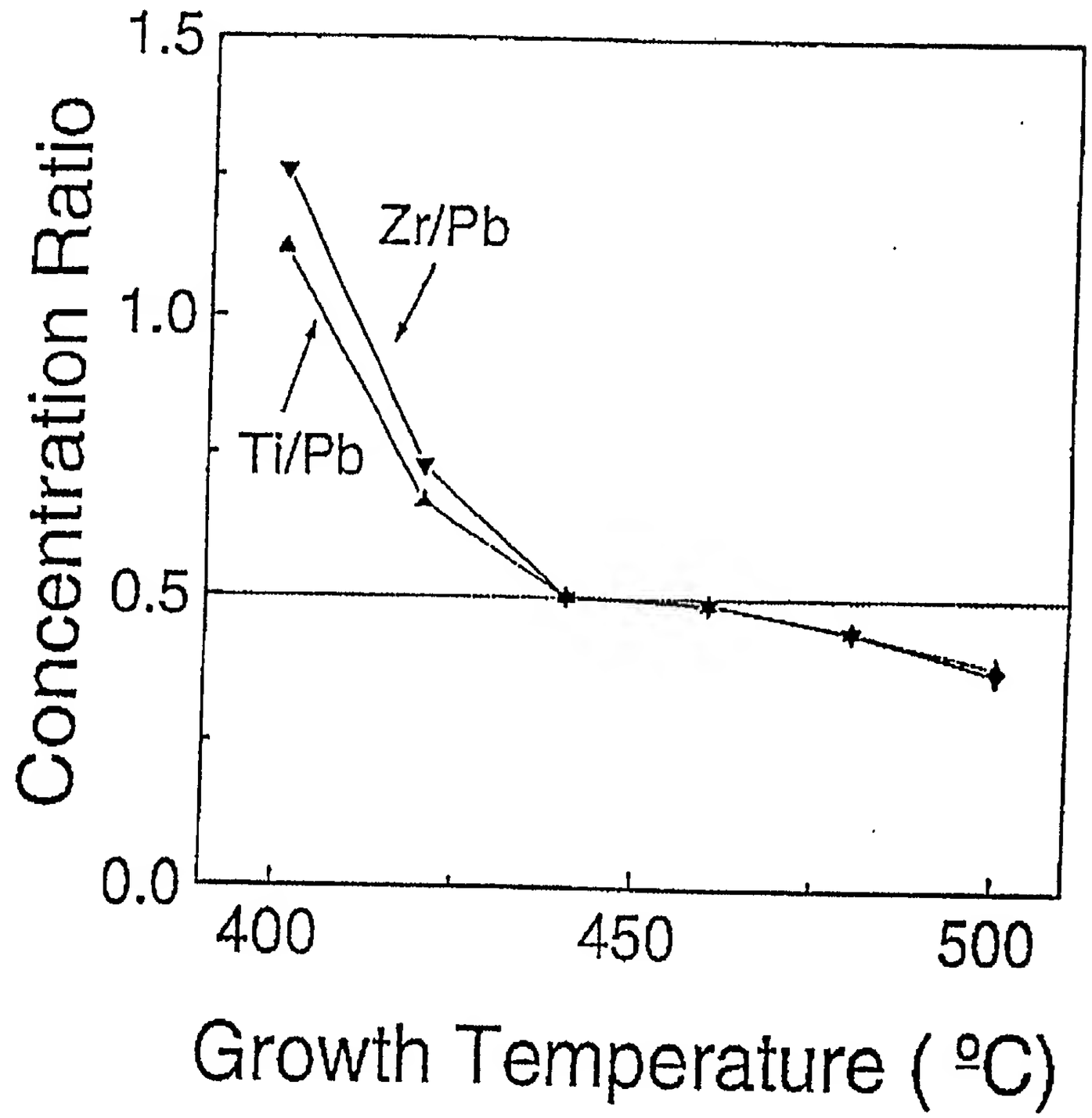


Fig. 25

Fig. 26



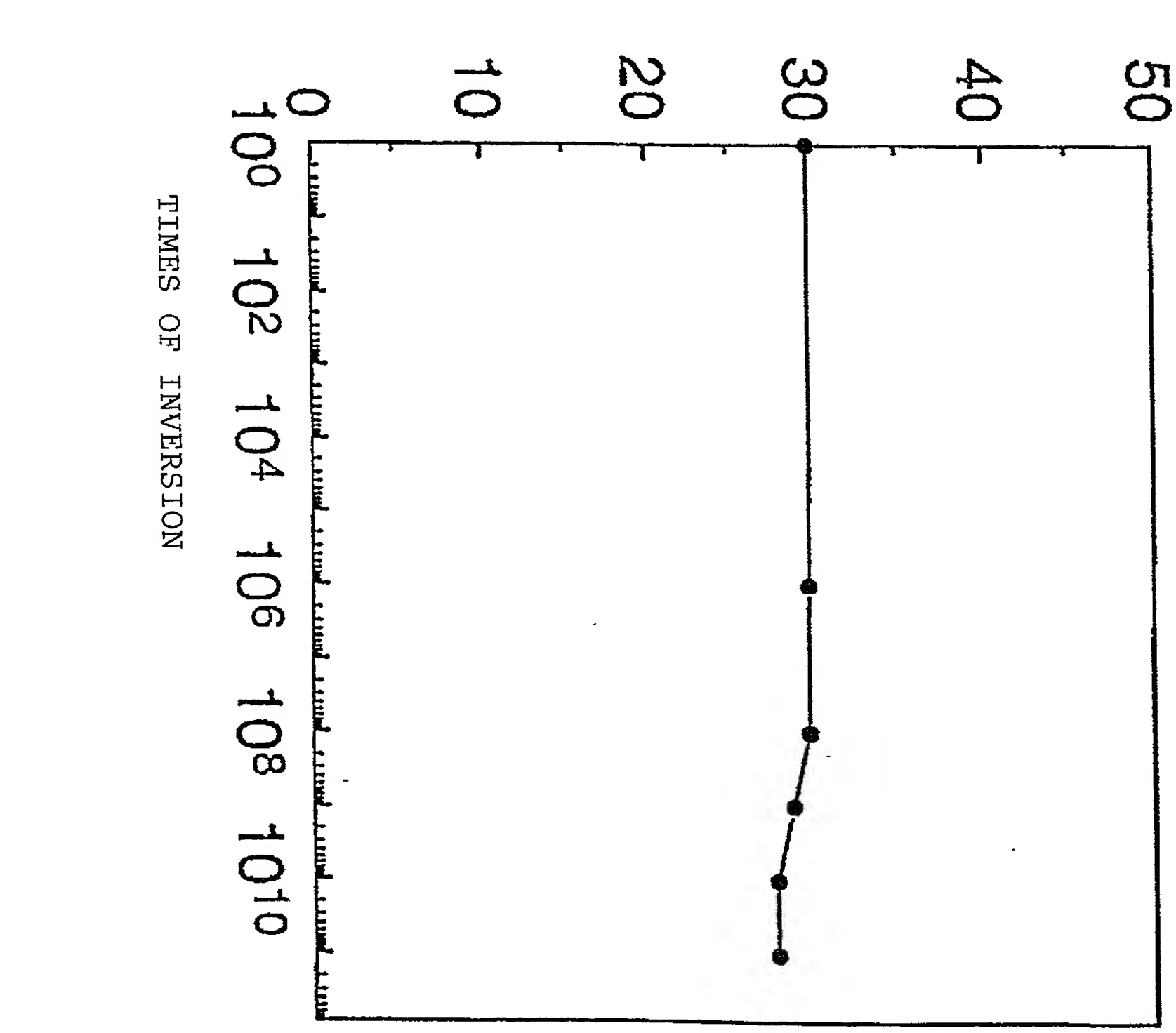

SPONTANEOUS POLARIZATION (μC/cm2)
50
40
30
20
10
0
10⁰ 10² 10⁴ 10⁶ 10⁸ 10¹⁰
TIMES OF INVERSION

Fig. 27

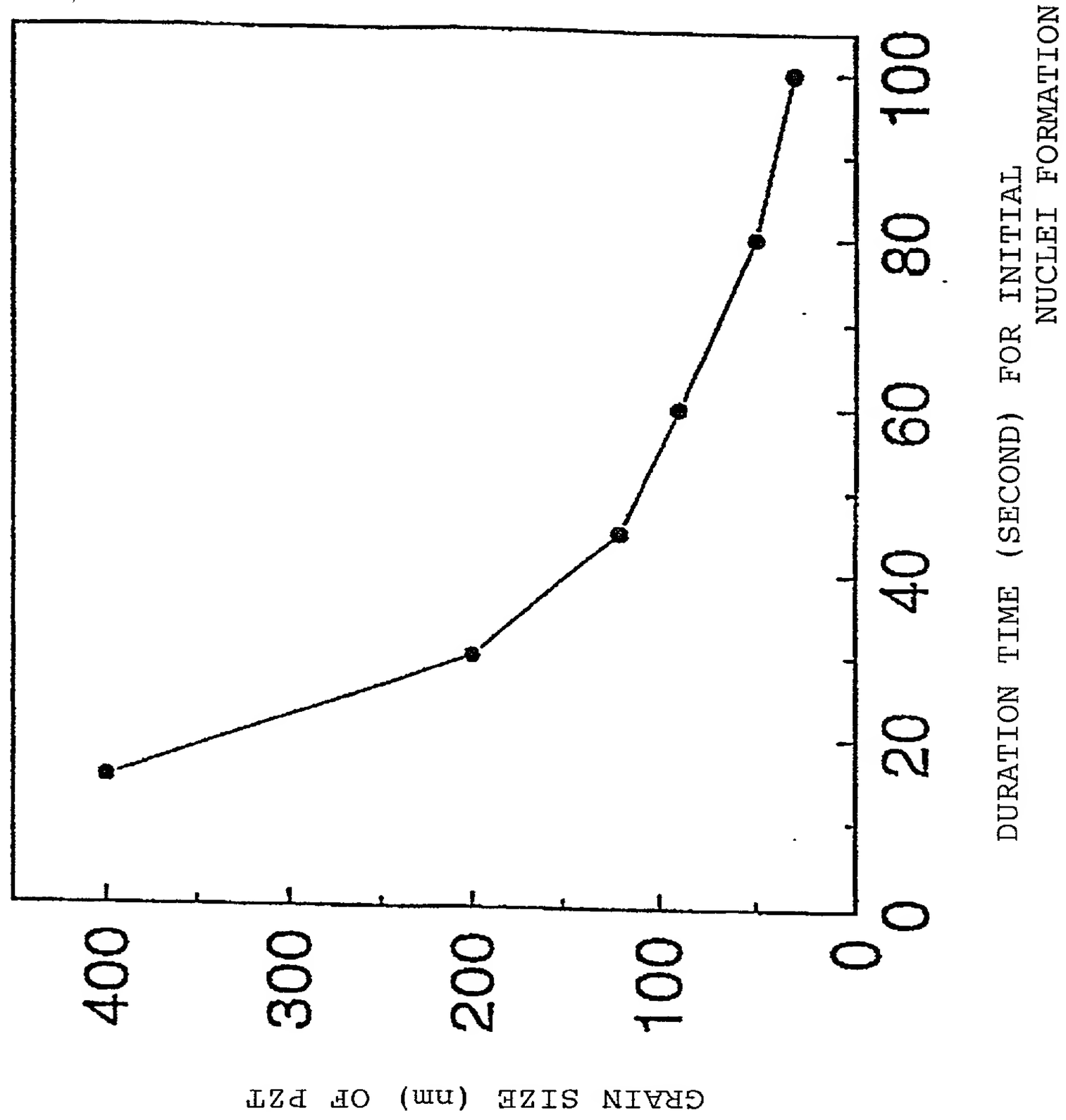


Fig. 28

Fig. 29 (A)

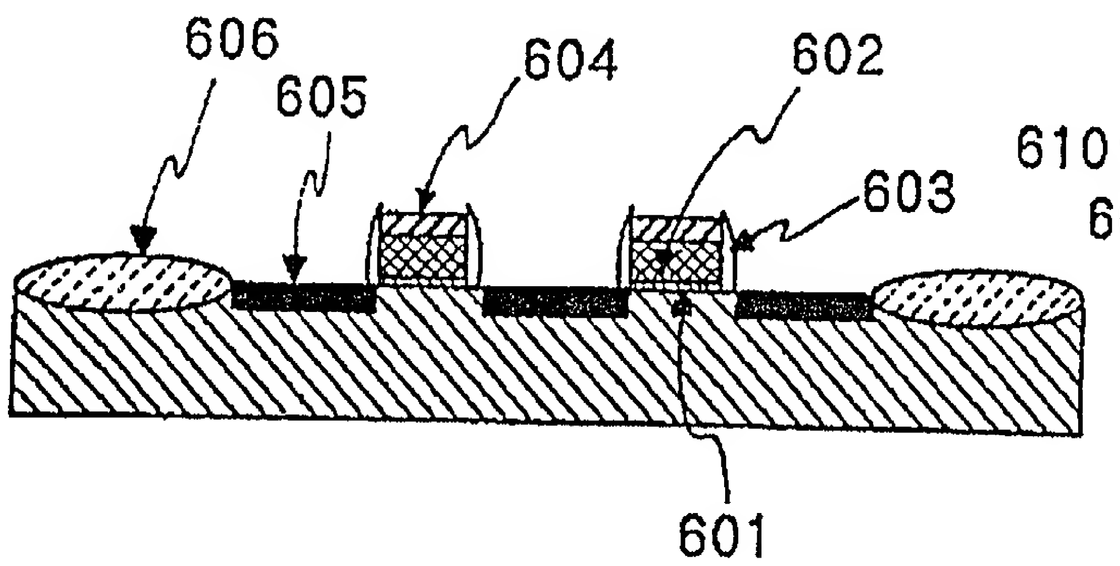


Fig. 29 (B)

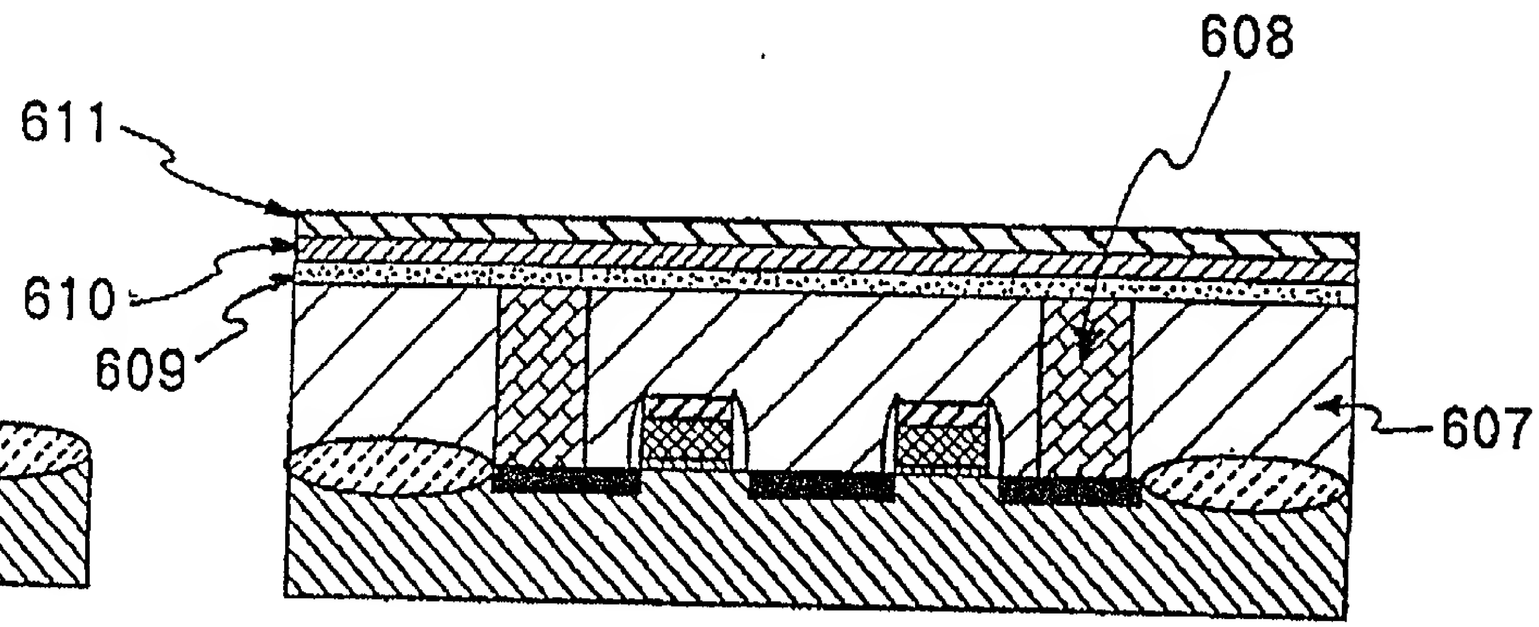


Fig. 29 (C)

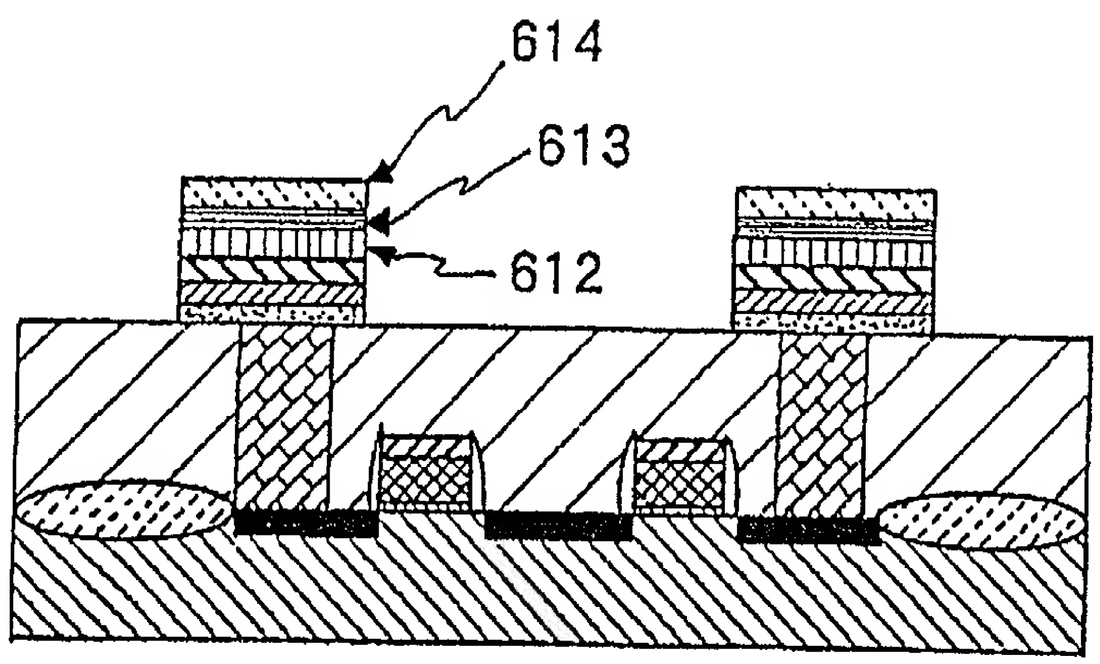


Fig. 29 (D)

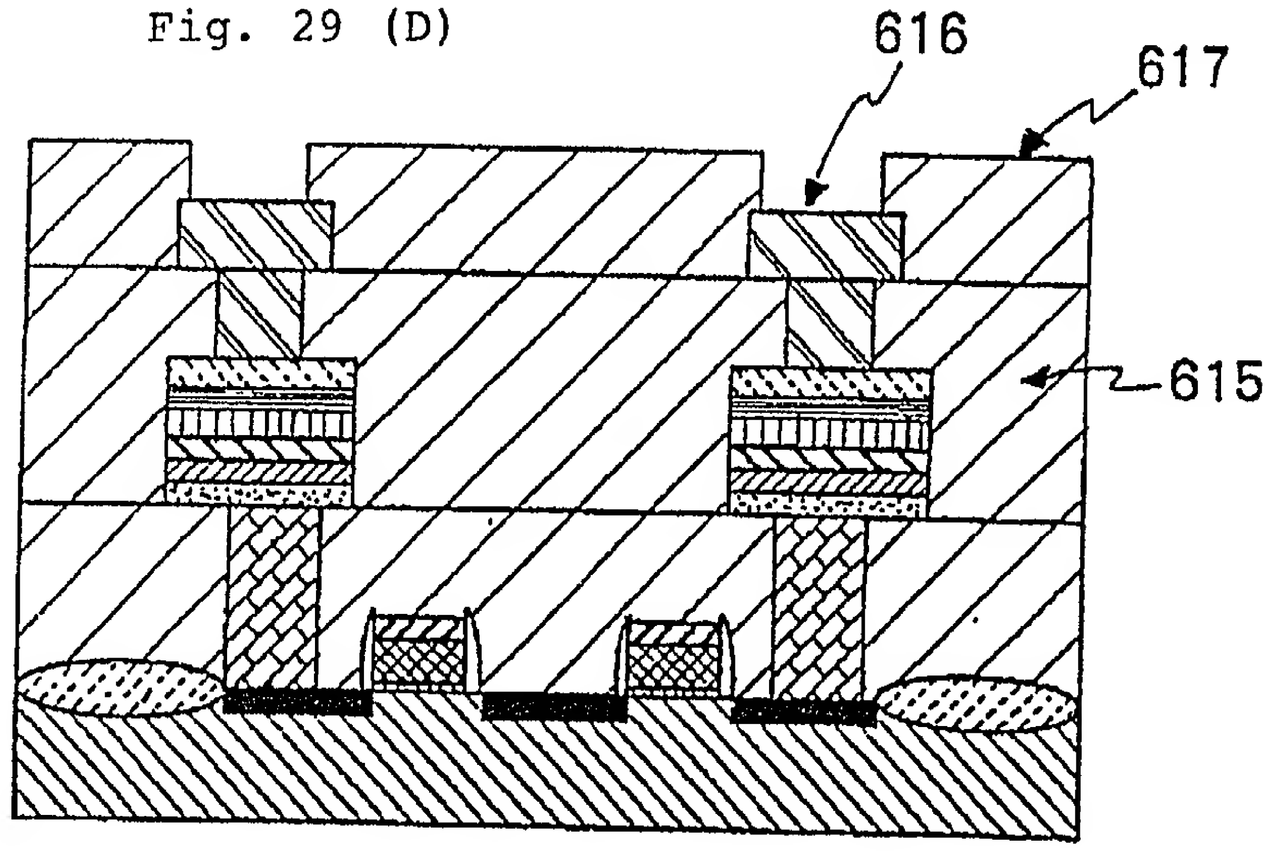


Fig. 30 (A)

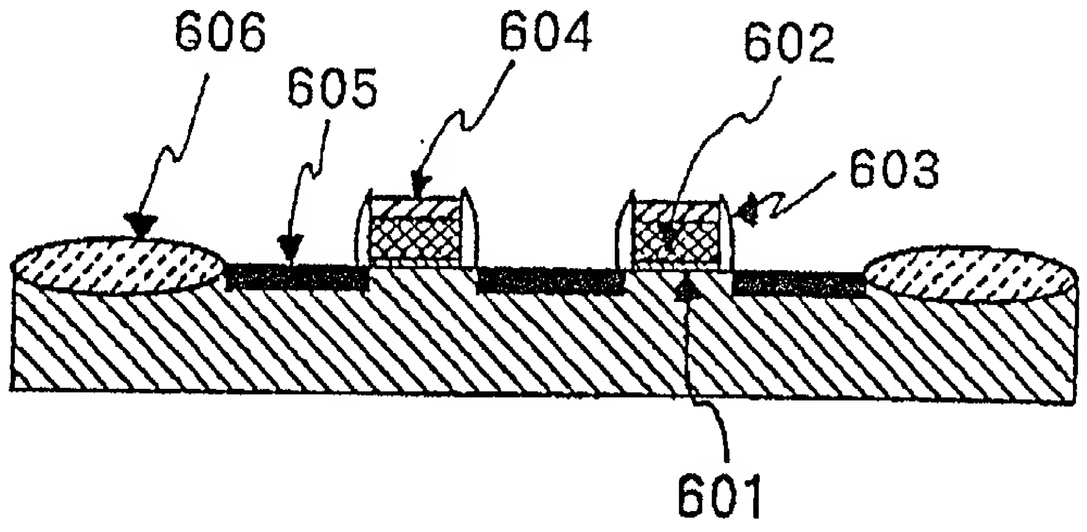


Fig. 30 (B)

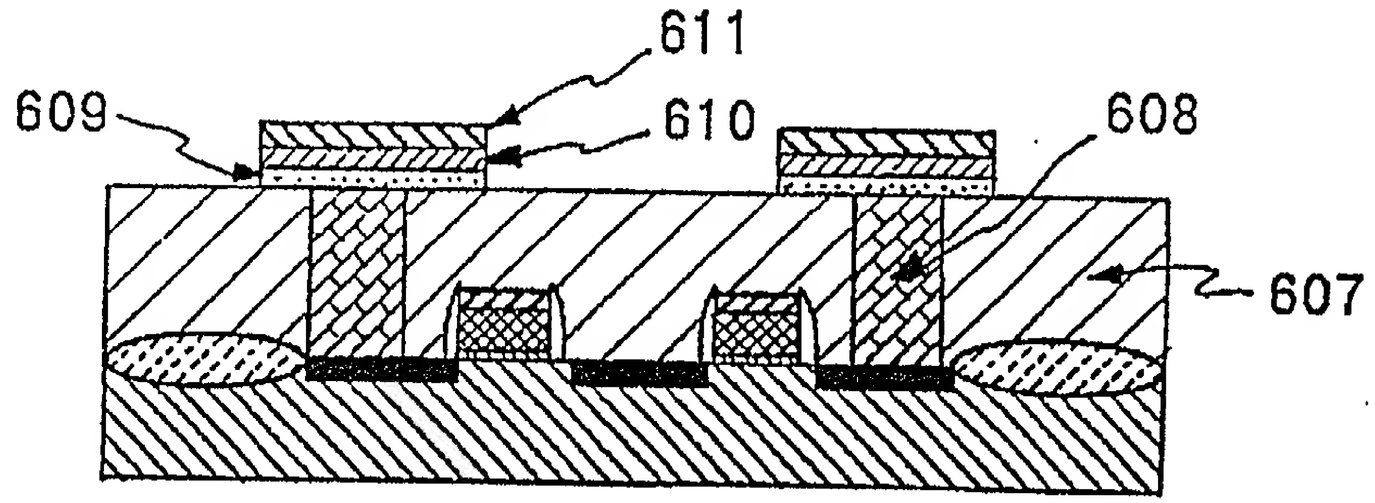


Fig. 30 (C)

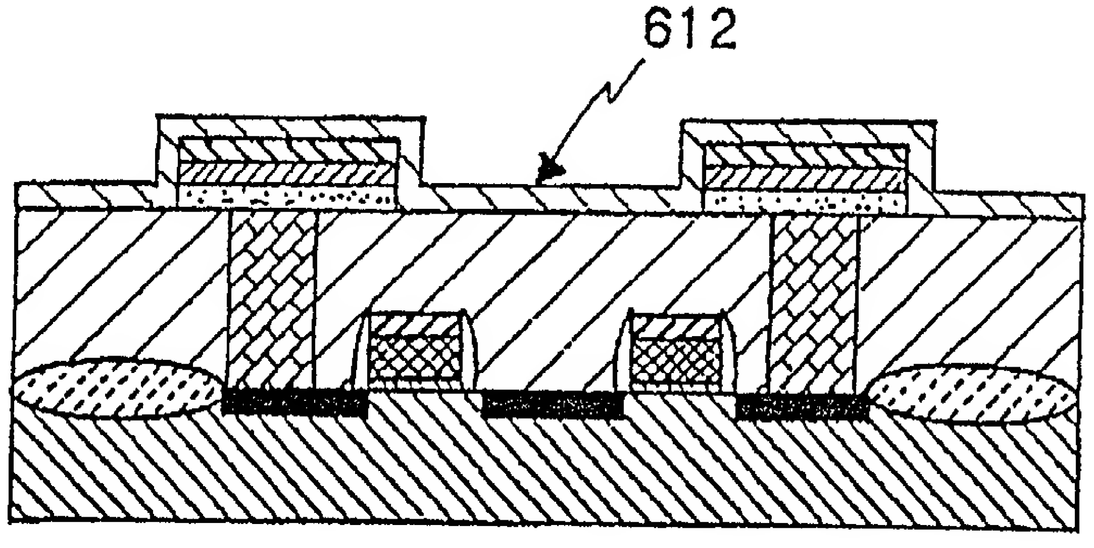


Fig. 30 (D)

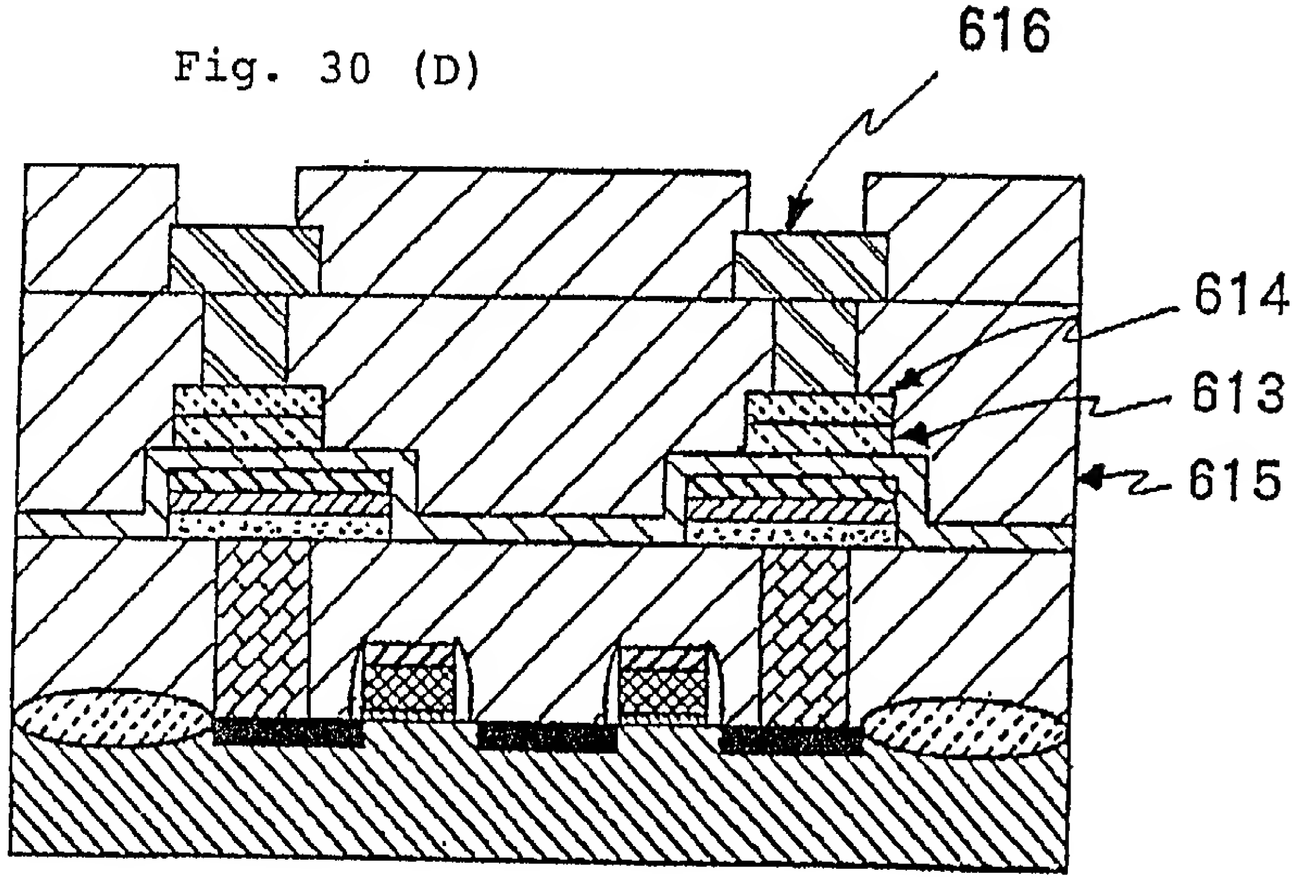


Fig. 31 (A)

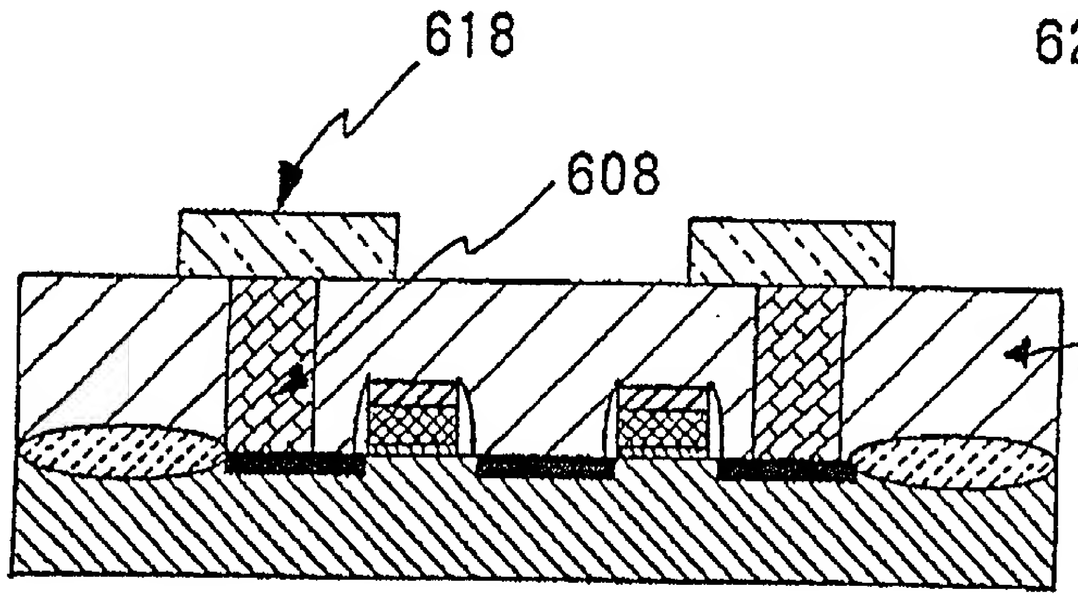


Fig. 31 (B)

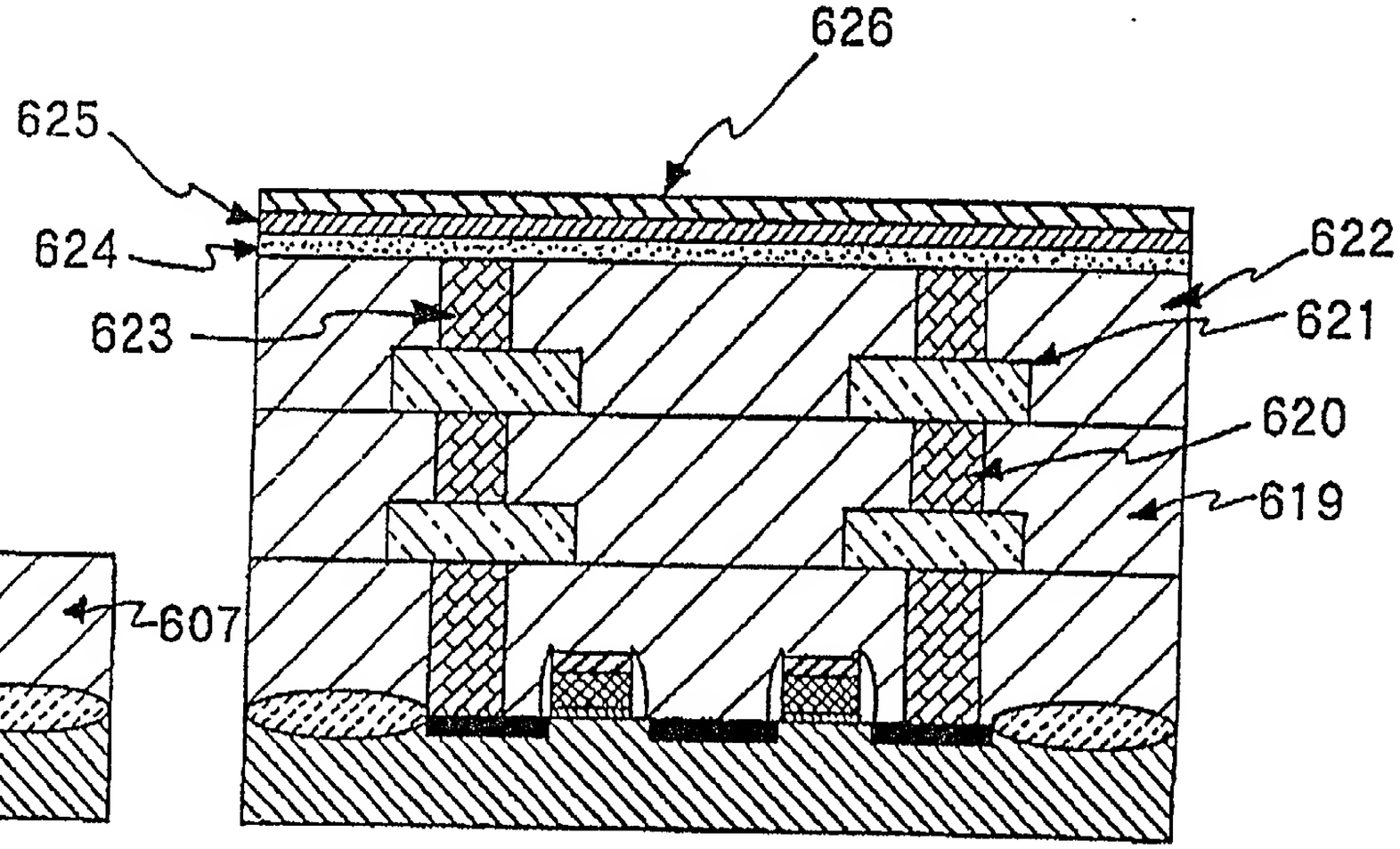


Fig. 32 (C)

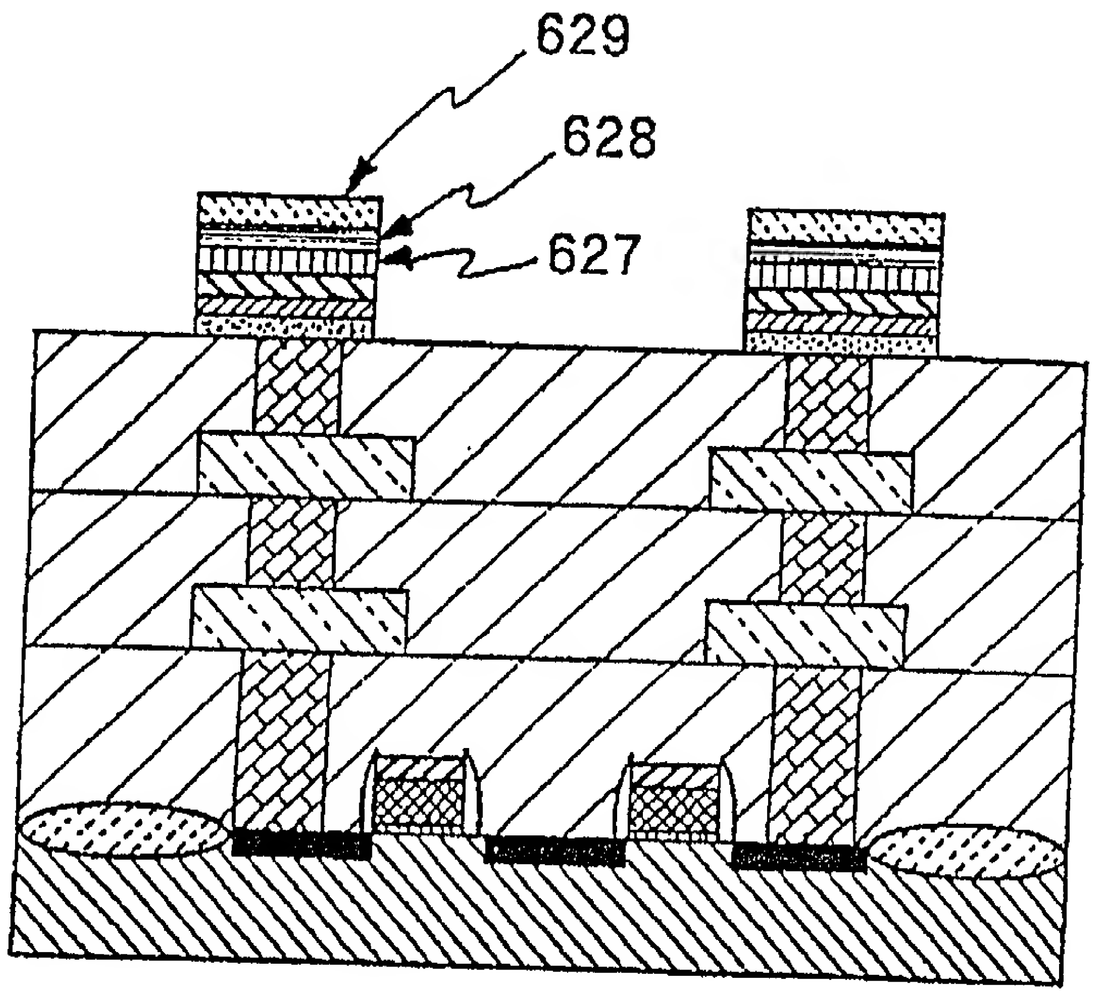
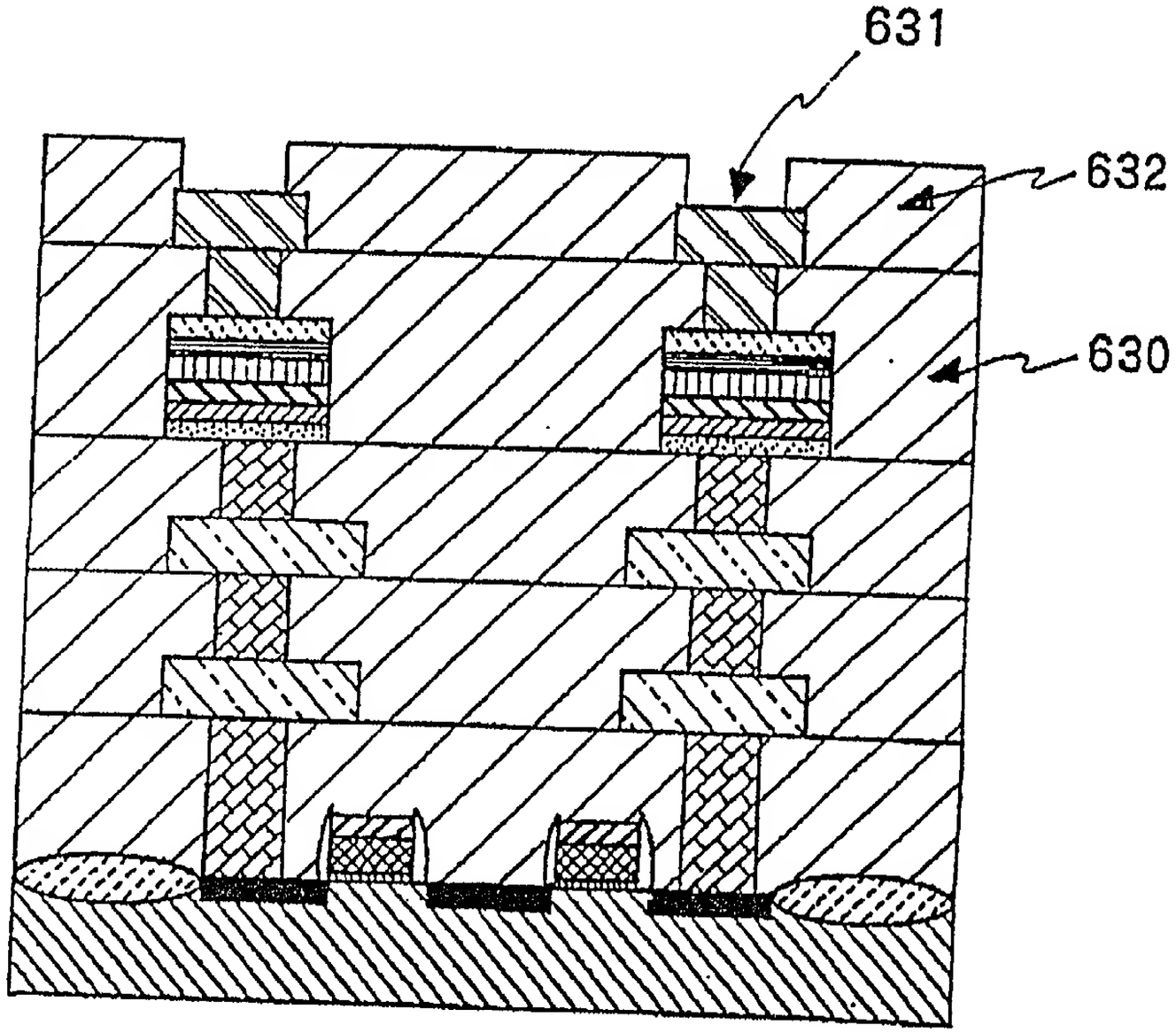


Fig. 32 (D)



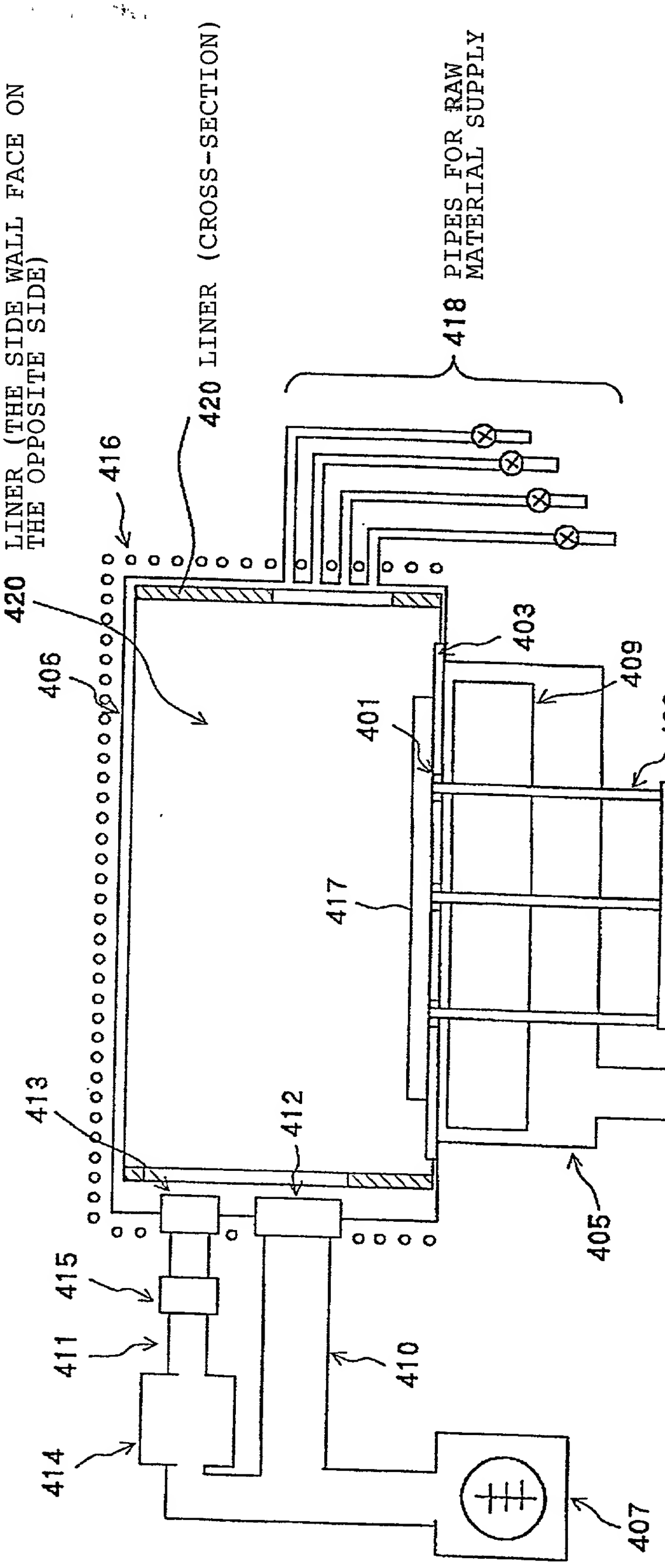
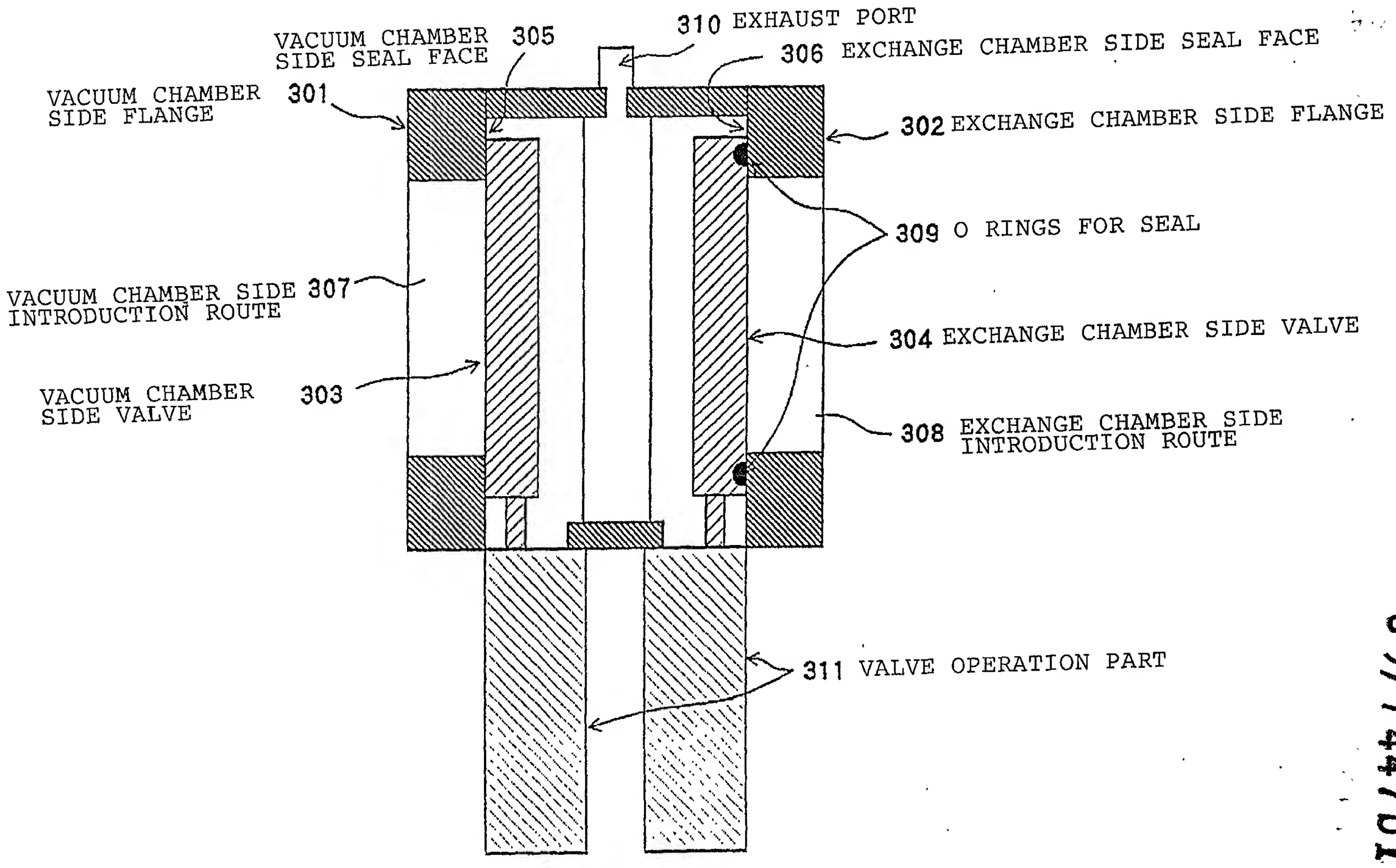

LINER (THE SIDE WALL FACE ON THE OPPOSITE SIDE)
420 LINER (CROSS-SECTION)
418 PIPES FOR RAW MATERIAL SUPPLY
416
420
406
413
412
415
411
414
410
401
402
403
409
417
405
408
407

Fig. 33

Fig. 34



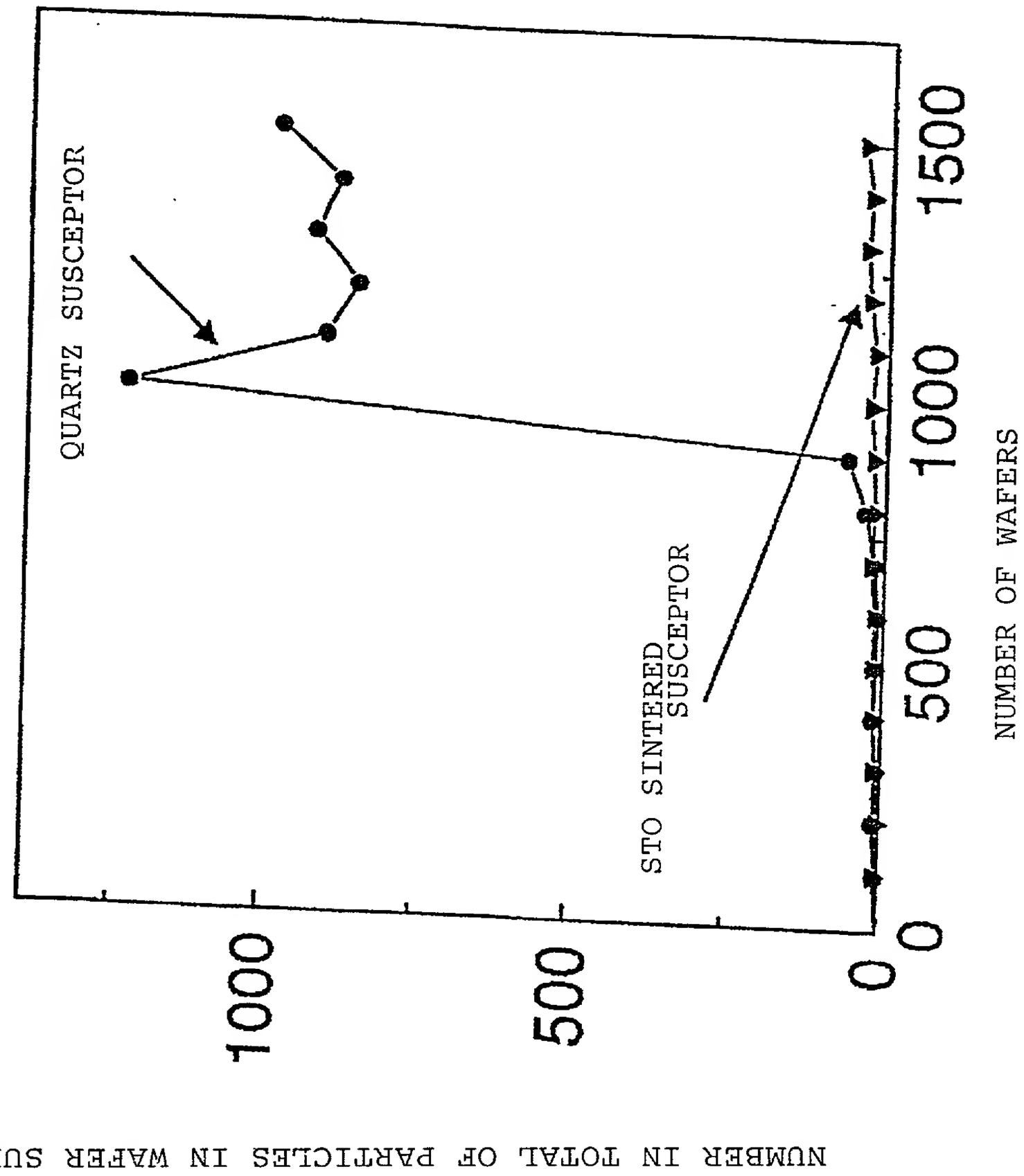

QUARTZ SUSCEPTOR
STO SINTERED SUSCEPTOR
1500
1000
500
0
0
500
1000
NUMBER OF WAFERS
NUMBER IN TOTAL OF PARTICLES IN WAFER SURFACE

Fig. 35

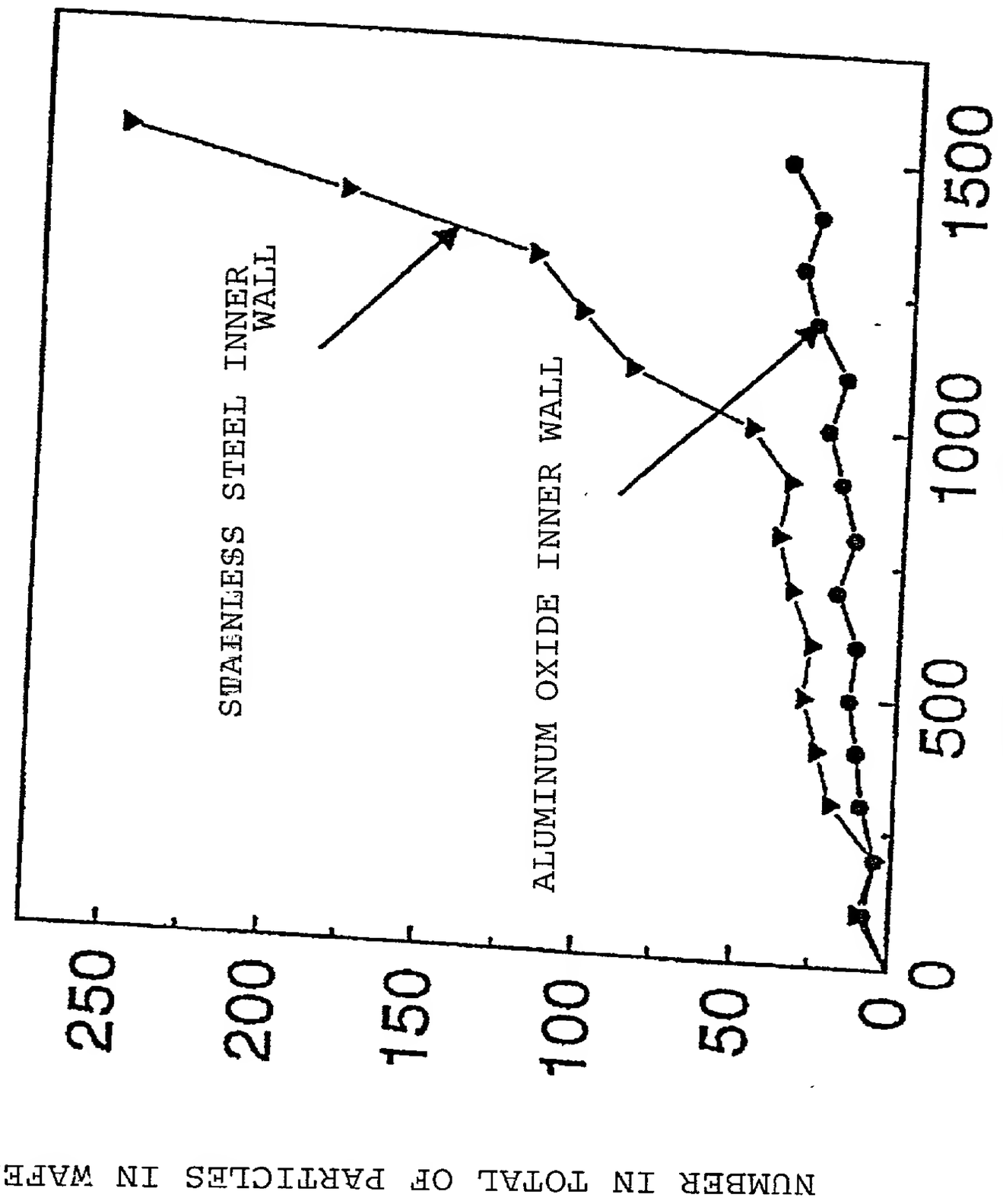

NUMBER IN TOTAL OF PARTICLES IN WAFER SURFACE
250
200
150
100
50
0
0
500
1000
1500
NUMBER OF WAFERS
STAINLESS STEEL INNER WALL
ALUMINUM OXIDE INNER WALL

Fig. 36

Filed Via Express Mail
Rec. No.: EL522399606US
On : January 29, 2001
By _____
Any fee due as a result of this paper, not covered by an enclosed check, may be charged on Deposit Acct. No. 08-1634.

Attorney Docket No.: NECW 18.281

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Inventors : **Toru TATSUMI, *et al.***

Filed : **Concurrently Herewith**

Title : **METHOD OF VAPOR PHASE GROWTH OF METAL OXIDE DIELECTRIC FILM AND APPARATUS FOR VAPOR PHASE GROWTH OF METAL OXIDE DIELECTRIC MATERIAL**

January 29, 2001

Assistant Commissioner for Patents
Box PCT
Washington, D.C. 20231

SUB-POWER OF ATTORNEY

S I R:

I, Aaron B. Karas, 18,923 attorney of record herein, do hereby grant a sub-power of attorney to Leonard Cooper, Reg. No. 27,625; Harris A. Wolin, Reg. No. 39,432; Linda S. Chan, Reg. No. 42,400; Brian Myers Reg. No. 46,947; Michael Markowitz, Reg. No. 30,659 to act and sign in my behalf in the above-referenced application.

Respectfully submitted

Aaron B. Karas; Reg. No. 18,923

HELFGOTT & KARAS, P.C.
EMPIRE STATE BUILDING - 60th Floor
NEW YORK, NEW YORK 10118-6098
(212) 643-5000
ABKdnh:18281power

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UNITED STATES

DECLARATION FOR PATENT APPLICATION Docket No. NECW 18.281

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled METHOD OF VAPOR PHASE GROWTH OF METAL OXIDE DIELECTRIC FILM AND APPARATUS FOR VAPOR PHASE GROWTH OF METAL OXIDE DIELECTRIC MATERIAL

the specification of which

(check one) [X] is attached hereto.

[ ] was filed on _____ as

Application Serial No. _____

and was amended on _____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by an amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s)			Priority Claimed
219183/1998 (Number)	Japan (Country)	03/08/1998 (Day/Month/Year Filed)	(Yes) No
219184/1998 (Number)	Japan (Country)	03/08/1998 (Day/Month/Year Filed)	(Yes) No
219187/1998 (Number)	Japan (Country)	03/08/1998 (Day/Month/Year Filed)	(Yes) No

I hereby claim the benefit under Title 35, United State Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.)	(Filing Date)	(Status - patented, pending, abandoned)
(Application Serial No.)	(Filing Date)	(Status - patented, pending, abandoned)

I hereby appoint as my attorney and agent Aaron B. Karas, Reg. No. 18,923, Samson Helfgott, Reg. No. 23,072 and Emma Shleifer, Reg. No. 29,734 to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

Address all correspondence to:

HELFGOTT & KARAS P.C.
60th Floor
Empire State Building
New York, New York 10118-0110
Telephone No. (212) 643-5000

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Full name of sole or first inventor Toru TATSUMI

Inventor's signature Toru Tatsumi Date January 19, 2001

Residence Tokyo, Japan Citizenship Japanese

Post Office Address c/o NEC Corporation, 7-1, Shiba 5-chome, Minato-ku, Tokyo 108-8001 Japan

Full name of second joint inventor, if any Atsushi YAMASHITA

Second Inventor's signature Atsushi Yamashita Date January 19, 2001

Residence Tokyo, Japan Citizenship Japanese

Post Office Address c/o NEC Corporation, 7-1, Shiba 5-chome, Minato-ku, Tokyo 108-8001 Japan